REACTION MECHANISM : PART-II

4.0 TYPE OF REACTIONS :

Reactions are of mainly four types :

1. Addition reactions.
2. Substitution reactions.
3. Elimination reactions.
4. Isomerisation reactions

4.1 ADDITION REACTIONS : It is also of three types :

(A) Electrophilic addition reactions

(B) Free radical addition reactions

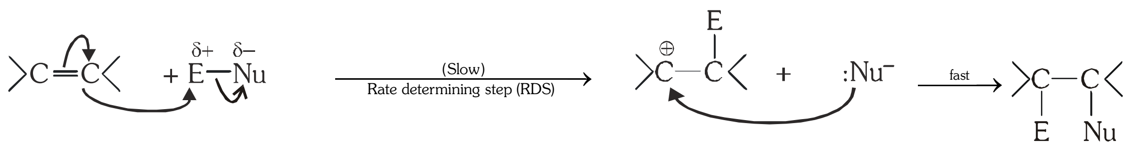
(C) Nucleophilic addition reactions

(A) Electrophilic addition reaction :- Because of the presence of >C=C< bond in molecules, alkenes generally take part in the ***addition reactions.***

$$\underset{\text{Alkene}}{>C=C<} \quad + \quad \underset{\text{Attacking molecule}}{AB} \longrightarrow \underset{\text{Addition product (Adduct)}}{-\underset{A}{\overset{|}{\underset{|}{C}}}-\underset{B}{\overset{|}{\underset{|}{C}}}-}$$

From mechanism point of view, the addition in alkenes is generally ***electrophilic in nature*** which means that attacking reagent which carries the initial attack is an electrophile (E^+). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds in two steps.

Step I : The π–electron cloud of the double bond causes the polarisation of the attacking molecule (E–Nu) which cleaves to release the electrophile (E^+) for the attack. The double bond simultaneously undergoes electromeric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a ***carbocation*** intermediate.



Addition product

Step II : The nucleophile ($:Nu^-$) released in the slow step combines with the carbocation to give the desired addition product in the fast step.

$$\boxed{\text{Reactivity for Electrophilic addition reaction} \propto \text{stability of carbocation formed in RDS}}$$

(1) Addition of Halogen : It is a electrophilic addition reaction.

$$R-CH=CH_2+X_2 \longrightarrow R-\overset{X}{\overset{|}{C}H}-\underset{X}{\underset{|}{C}H_2}$$

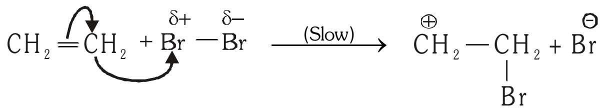
(Vicinal halides)

(a) The addition of Br_2 on alkenes provides a useful test for unsaturation in molecule. The brown colour of the bromine being rapidly discharged. Thus decolarization of 5% Br_2 in CCl_4 by a compound suggest unsaturation in it. Colourless dibromo compound is formed.

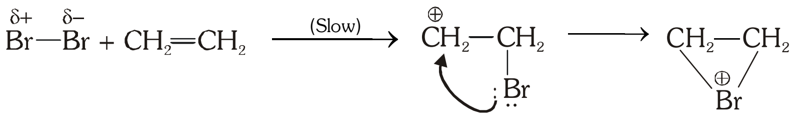
(b) I_2 reacts with alkenes to form Vicinal di-iodides which are unstable and I_2 gets eliminated to give original alkene.

$$CH_3-CH=CH_2 + I_2 \rightleftharpoons CH_3-\overset{I}{\overset{|}{C}H}-\underset{I}{\underset{|}{C}H_2}$$

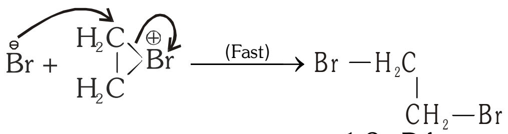
Unstable

Mechanism : 

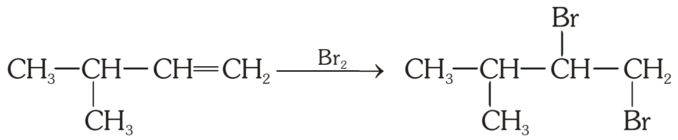
It is interesting to note that product which is mainly formed as a result of addition is ***trans*** in nature whereas the cis isomer is obtained in relatively smaller proportions. Since carbocation intermediate is planar (sp^2 hybridised), both cis and trans addition products must be formed almost in equal proportions. The trans product can be justified in case a cyclic halonium ion is formed by the initial electrophile attack.



(Halonium ion)



1,2,–Dibromoethane (Anti)

Eg. 

Anti addition

No carbocation rearrangement and anti addition product.

(2) Addition of halogen acid :

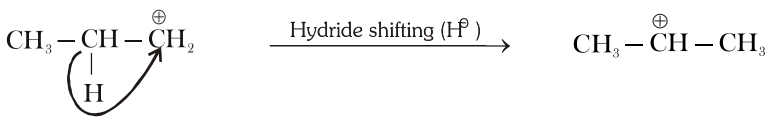
$$R-CH=CH-R + HX \longrightarrow R-CH_2-\underset{}{CH}(X)-R$$

$$R-CH=CH_2 + HX \longrightarrow R-CH(X)-CH_3$$

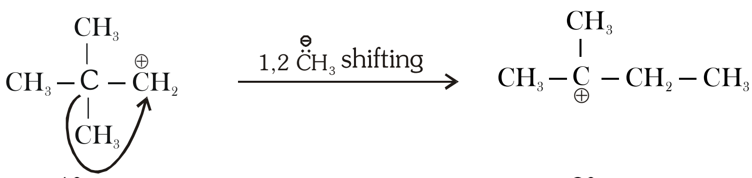
GOLDEN KEY POINTS

- The order of reactivity of hydrogen halide is : **HI > HBr > HCl**
- Addition on alkene proceeds via the formation of more stable carbonium ion.
- Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markovnikov's rule. Carbocation rearrangement is observed in the reaction.

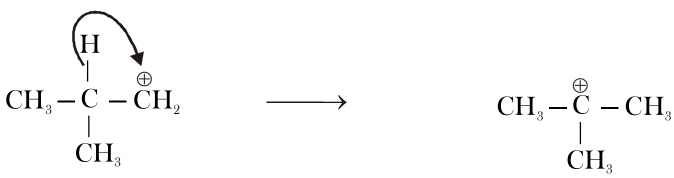
Rearrangement in carbocation

Ex. 

1° (less stable) 2° (more stable)

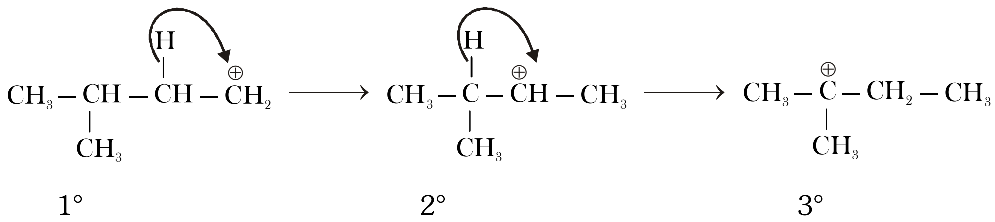
Ex. 

1° 3°

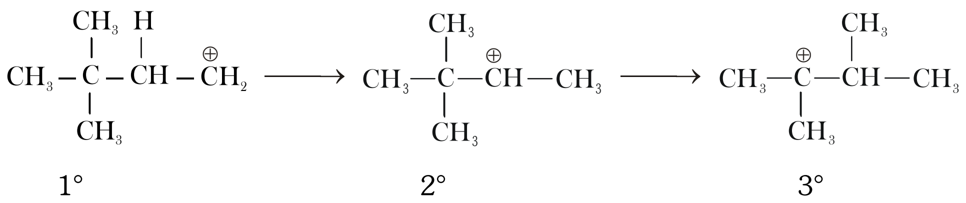
Ex. 

1° 3°

Ex.



Ex.



Markovnikov's Rule States :

(a) ***First Rule :*** When molecule of HX add up on unsymmetrical unsaturated hydrocarbon, the electrophile (H^+) goes to the unsaturated carbon atom bearing more number of hydrogen atoms.

$$CH_3—CH{=}CH_2 + HX \longrightarrow CH_3—\underset{}{\overset{X}{\overset{|}{C}H}}—\underset{\underset{H}{|}}{CH_2}$$

Mechanism : It is electrophilic addition and is illustrated by the action of HCl to propene.

$$CH_3—CH{=}CH_2 + \overset{\delta+}{H}—Cl \xrightarrow{\text{Slow}} CH_3—\overset{\oplus}{C}H—CH_3 + Cl^-$$

Secondary carbocation

$$Cl^- + CH_3—\overset{\oplus}{C}H—CH_3 \xrightarrow{\text{Fast}} CH_3—\underset{\underset{Cl}{|}}{CH}—CH_3$$

2–Chloropropane

Primary carbocation ($CH_3—CH_2—\overset{\oplus}{C}H_2$) is also formed but only in very small proportion since it is less stable than the secondary carbocation. Markovnikov's rule is based on stability of carbocation.

Note ; The electrophilic addition of HX to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

(b) ***Second Rule :*** In the addition of HX to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.

$$CH_2{=}CH—Cl + HCl \longrightarrow CH_3—\underset{\underset{Cl}{|}}{CH}—Cl$$

Ethylidene chloride

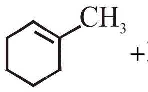
Mechanism : $CH_2{=}CH—\ddot{\underset{..}{Cl}}: \xrightarrow{\overset{\oplus}{H}} CH_3—\overset{\oplus}{C}H—\ddot{\underset{..}{Cl}} \xrightarrow{\overset{\ominus}{Cl}} CH_3—\overset{\overset{Cl}{|}}{C}H—Cl$

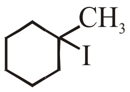
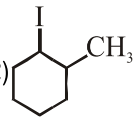
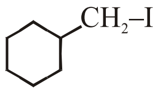
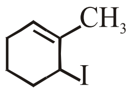
All polar reagents of the general structure $\overset{\oplus}{Y}\,\overset{\ominus}{Z}$ (such as $\overset{\oplus}{H}—\overset{\ominus}{X}$, $\overset{\oplus}{H}—\overset{\ominus}{OH}$ $\overset{\oplus}{H}—\overset{\ominus}{SO_3H}$, $\overset{\oplus}{X}\,\overset{\ominus}{OH}$) add on unsymmetrical unsaturated compound in accordance with Markovnikov's rules. Such additions are called normal Markovnikov's rule, where as additions in the opposite manner are referred to as abnormal or ***anti Markovnikov's additions.***

BEGINNER'S BOX-1

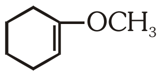
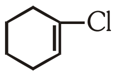
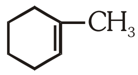
1. The intermediate in the Electrophilic addition–reaction is :-

(1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

2.  $+HI \longrightarrow$ major product is

(1)  (2)  (3)  (4) 

3. Give reactivity order towards EAR.

(i)  (ii)  (iii)  (iv) 

(1) (i) > (ii) > (iii) > (iv)
(2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (iv) > (i) > (iii)
(4) (iii) > (ii) > (iv) > (i)

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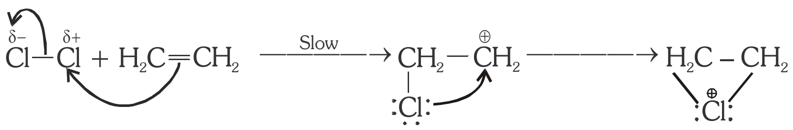
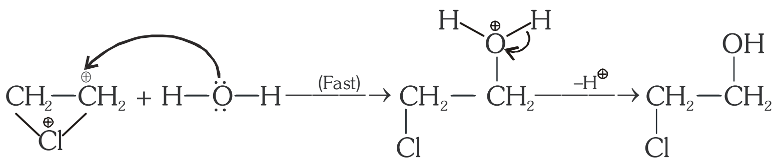
(3) Addition of Hypohalous acid (or X_2/H_2O, or HOX) : It is a electrophilic addition and follows Markovnikov's rule, and anti addition.



Carbocation



Ethylene chlorohydrin

$$R-C\equiv CH + HOCl \longrightarrow R-\underset{\underset{O}{\|}}{C}-CHCl_2$$

(4) Addition of water (Hydration of alkenes) : Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as acidic **hydration reaction**. Intermediate in this reaction is carbocation, so rearrangement may take place.

(i) $$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O \xrightarrow{H^+} \underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$

(ii) $$\underset{\text{2–Methylpropene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} + H_2O \xrightarrow{H^+} \underset{\text{2-Methylpropan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

Mechanism :

$$CH_3-CH=CH_2 + H^+ \xrightarrow{(Slow)} CH_3-\overset{\oplus}{C}H-CH_3$$

Carbocation (2°)

$$CH_3-\overset{\oplus}{C}H-CH_3 + H-\ddot{O}-H \xrightarrow{\text{(Fast)}} CH_3-\underset{\underset{\oplus}{H-\ddot{O}-H}}{\underset{|}{C}H}-CH_3 \xrightarrow{-H^+} CH_3-\underset{O-H}{\underset{|}{C}H}-CH_3$$

Propan-2-ol

(5) Addition of NOCl (Tilden reagent) : $CH_3-CH=CH_2 + \overset{\delta+}{N}\overset{\delta-}{OCl} \longrightarrow CH_3-\overset{Cl}{\overset{|}{C}H}-\overset{NO}{\overset{|}{C}H}$

Propylene nitrosochloride

(6) Hydroboration Oxidation : Borane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.

$$R-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 + BH_3 \xrightarrow{\text{T.H.F.}} (R-CH_2-CH_2)BH_2$$

$$(R-CH_2-CH_2)BH_2 \xrightarrow{R-CH=CH_2} (R-CH_2-CH_2)_2BH$$

$$(R-CH_2-CH_2)_2BH \xrightarrow{R-CH=CH_2} (R-CH_2-CH_2)_3B$$

Trialkylborane

BH_3 does not exist freely as monomer so a solvent THF (tetra hydro furane) is used to stabilised it.

Ex. $3CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 + \overset{\delta+}{B}\overset{\delta-}{H_3} \xrightarrow{\text{THF}} (CH_3-CH_2-CH_2)_3B$

BHR_2 also can be taken.

Ex. $CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 + BHR_2 \longrightarrow CH_3-CH_2-CH_2-BR_2$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O/H^+} 3CH_3-CH_2-CH_3 + H_3BO_3$$

(Tripropyl Borane) → Propane

$$(CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O_2/\overset{\ominus}{O}H} CH_3-CH_2-CH_2-OH$$

Propanol (1° alcohol)

$$3R-C\equiv C-R \xrightarrow[\text{THF}]{BH_3} (R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-)_3B$$

$$R-\overset{\delta+}{C}\equiv\overset{\delta-}{C}-R + \overset{\delta+}{B}\overset{\delta-}{H_3} \longrightarrow R-CH=\underset{R}{\underset{|}{C}}-BH_2$$

$$R-CH=\underset{R}{\underset{|}{C}}-BH_2 + 2R-C\equiv C-R \longrightarrow (R-CH=\underset{R}{\underset{|}{C}}-)_3B$$

$$(R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-)_3B \xrightarrow[\text{Basic oxidation}]{H_2O_2/(\overset{\ominus}{O}H)} (R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-OH + H_3BO_3 \longrightarrow R-CH_2-\underset{O}{\underset{\|}{C}}-R$$

(enol form) (Ketones)

$$(R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-)_3B \xrightarrow{H^+/H_2O} \underset{H}{\overset{R}{C}}=\underset{H}{\overset{R}{C}} + H_3BO_3$$

(cis-Alkene)

Note : The overall process appears to be addition of water according to anti Markovnikov's rule and involves syn. addition.

(7) Oxymercuration – demercuration : Mercuric acetate in water is treated with an alkene. The addition product on reduction with sodium Boro hydride in aqueous NaOH Solution gives alcohol. It follows the Markovnikov's rule.

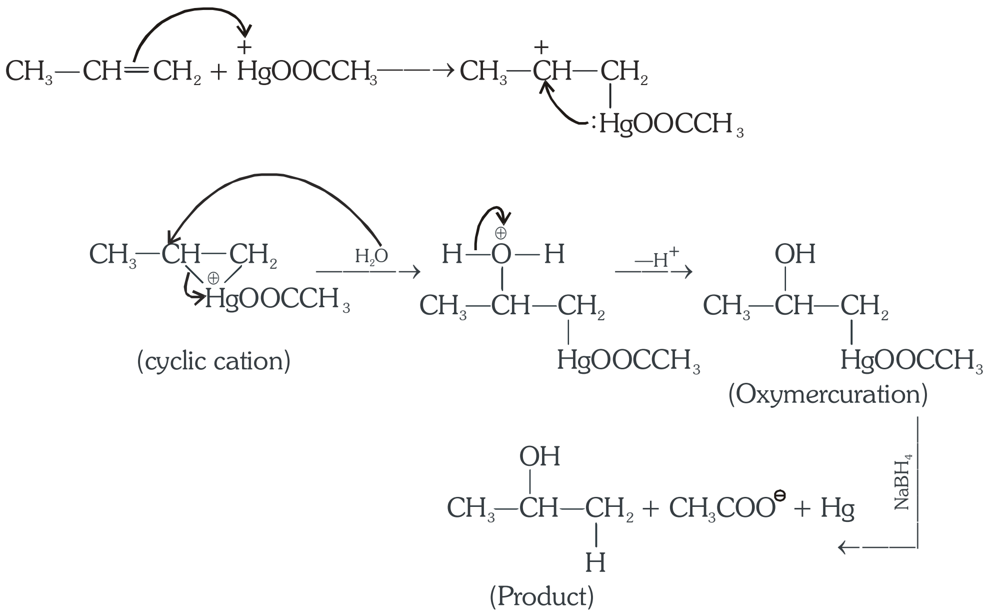
$$CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3$$

(i) $(AcO)_2$ Hg/H_2O (Mercuric acetate) or $(CH_3COO)_2$ Hg/H_2O

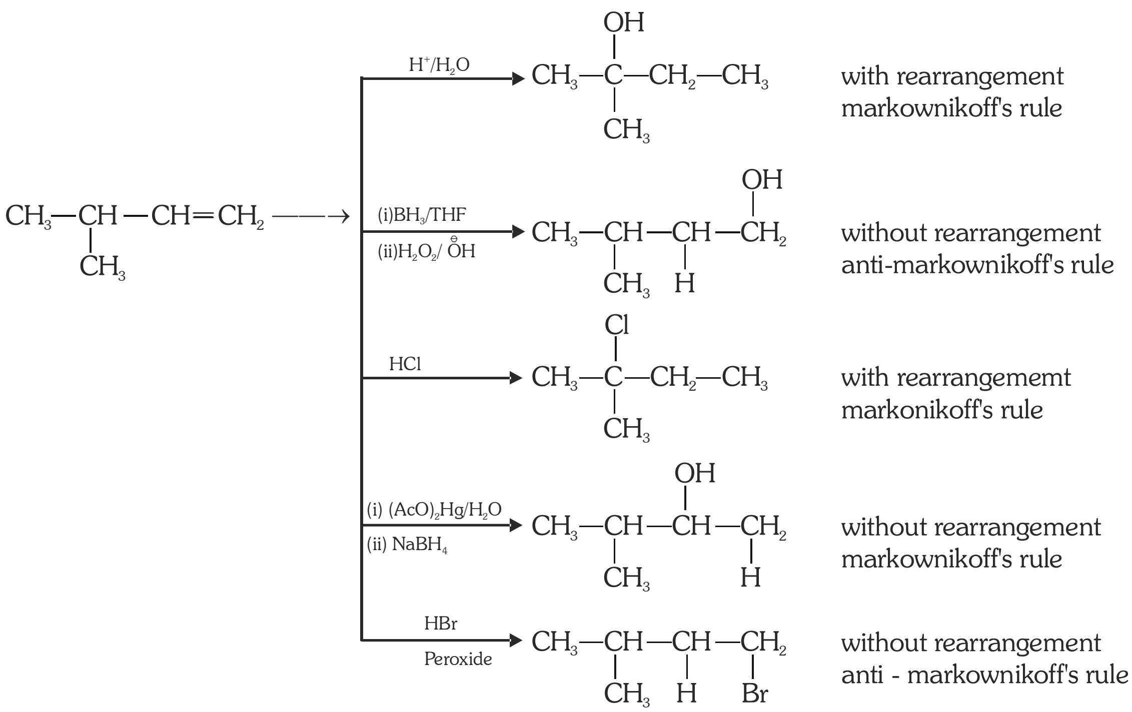
(ii) $NaBH_4$

Mechanism :

$$\begin{matrix} CH_3{-}COO \\ CH_3{-}COO \end{matrix}\!\!>Hg \xrightarrow{H_2O} CH_3{-}COO^- + CH_3{-}COOHg^+ \text{ (Electrophile)}$$



Note : Intermediate is cyclic cation so there is no rearrangement.



BEGINNER'S BOX-2

1. What is the product formed when acetylene reacts with hypochlorous acid ?

(1) CH_3COCl (2) $ClCH_2CHO$ (3) Cl_2CHCHO (4) $ClCH_2COOH$

2. Primary alcohol can be formed as major product by

(1) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH_2 \xrightarrow[(2)H_2O_2/\overset{\ominus}{O}H]{(1)BH_3,THF}$ (2) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{dil.H_2SO_4}$

(3) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[(2)NaBH_4]{(1)(CH_3COO)_2Hg,H_2O}$ (4) 2 & 3 both

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(B) Free radical addition reactions :- Addition of HBr on alkene or alkyne in presence of peroxide.

$$CH_3-CH=CH_2 \xrightarrow[ROOR]{HBr(\Delta)} CH_3-\underset{H}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

Anti Markovnikov's rule or peroxide effect or Kharasch rule

(i) In the presence of peroxides the addition of HBr on unsaturated unsymmetrical compound takes place contrary to Markovnikov's rule. This is called peroxide effect and is due to the difference in the mechanism of the addition.

(ii) In the normal Markovnikov's addition the mechanism is ionic.

(iii) In the presence of peroxide the addition of HBr takes place via free radicals.

(iv) Peroxide effect is not observed in case of H–F, HCl and HI. Reactions follows electrophilic addition mechanism.

$$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$$

Isopropyl bromide — Markownikoff's addition.

$$CH_3-CH=CH_2 \xrightarrow[R-O-O-R]{HBr} CH_3-CH_2-CH_2-Br$$

n–Propyl bromide — Anti Markownikoff's addition

Mechanism :

(i) Chain initiation -

(a) $R-O-O-R \longrightarrow 2RO^{\bullet}$

$$\boxed{HBr + RO^{\bullet} \longrightarrow ROH + Br^{\bullet}}$$

(ii) Chain propagation

$$CH_3-CH=CH_2 + \overset{\bullet}{Br} \longrightarrow CH_3-\overset{\bullet}{C}H-CH_2Br \xrightarrow{HBr} CH_3CH_2CH_2Br + \overset{\bullet}{Br}$$

2° free radical more stable (major)

$$CH_3-CH=CH_2 + \overset{\bullet}{Br} \longrightarrow CH_3-\overset{Br}{\overset{|}{C}H}-\overset{\bullet}{C}H_2 \xrightarrow{HBr} CH_3\overset{Br}{\overset{|}{C}H}CH_3 + \overset{\bullet}{Br}$$

1° free radical less stable

(iii) Chain termination :

$$R-\overset{\bullet}{C}H-CH_2-Br + Br^{\bullet} \longrightarrow R-CH(Br)-CH_2(Br)$$

$$R-\overset{\bullet}{C}H-CH_2-Br + R-\overset{\bullet}{C}H-CH_2-Br \longrightarrow \begin{array}{l} R-CH-CH_2-Br \\ \quad\;\;| \\ R-CH-CH_2-Br \end{array}$$

$${}^{\bullet}Br + {}^{\bullet}Br \longrightarrow Br-Br$$

Question : $CH_3-CH=CH_2 \xrightarrow[ROOR]{HCl} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$

Ans. no effect simple EAR

(C) Nucleophilic Addition Reaction :-

(C_1) NAR in Alkyne : In these reactions some heavy metal cation like Hg^{+2}, Pb^{+2}, Ba^{+2} are used. These cation attracts the π^- e^- of alkynes and decrease the e^- density and hence a nucleophile can attack an alkynes.

(1) Addition of dil. H_2SO_4 (Hydration) : The addition of water takes place in the presence of Hg^{+2} and H_2SO_4 [1% $HgSO_4$+40% H_2SO_4].

$$CH\equiv CH + H-OH \longrightarrow \underset{\text{(Enol)}}{CH_2=CH-OH} \rightleftharpoons CH_3-CHO$$

$$CH_3-C\equiv CH + H-OH \longrightarrow \underset{\text{enol}}{CH_3-\overset{\overset{OH}{|}}{C}=\overset{\overset{H}{|}}{CH}} \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Mechanism :

$$R-C\equiv CH \xrightarrow{Hg^{+2}} R-\overset{\oplus}{C}=\underset{\underset{:Hg^+}{|}}{CH} \longrightarrow R-\underset{\underset{Hg}{\cdot\cdot^{+2}\cdot\cdot}}{C=CH}$$

$$R-\underset{\underset{Hg}{+2}}{C=CH} \xrightarrow{H-\ddot{O}-H} R-\overset{\overset{H-\overset{+}{O}-H}{|}}{C}=\underset{\underset{Hg^+}{|}}{CH} \xrightarrow{-H^+} R-\overset{\overset{OH}{|}}{C}=\underset{\underset{Hg^+}{|}}{CH} \xrightarrow[-Hg^{+2}]{H^+} \underset{\text{(enol)}}{R-\overset{\overset{OH}{|}}{C}=\underset{\underset{H}{|}}{CH}} \longrightarrow \underset{\text{(Keto more stable)}}{R-\underset{\underset{O}{\|}}{C}-CH_3}$$

Ex. $$CH_3-C\equiv C-CH_3 \xrightarrow[Hg^{+2}]{H^+/H_2O} CH_3-\overset{\overset{OH}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

2-butanone

(2) Addition of alcohols : In presence of BF_3 and HgO alkynes react with alcohols and form acetal and ketal

$$CH\equiv CH + CH_3OH \xrightarrow[HgO]{BF_3} CH_2=CHOCH_3 \xrightarrow{CH_3OH} CH_3-CH\langle\begin{smallmatrix}OCH_3\\OCH_3\end{smallmatrix}$$

Methylal (acetal)

$$R-C\equiv CH + CH_3-OH \xrightarrow[HgO]{BF_3} R-\overset{\overset{OCH_3}{|}}{C}=CH_2 \xrightarrow{CH_3OH} R-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_3$$

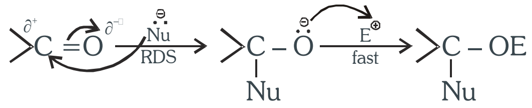
Ketal

(3) Addition of $AsCl_3$: In presence of $AlCl_3$ or $HgCl_2$ acetylene combines with $AsCl_3$ to yield Lewisite gas. It is four times poisonous than mustard gas.

$$CH\equiv CH + Cl-AsCl_2 \longrightarrow \underset{\underset{CHAsCl_2}{\|}}{CH-Cl}$$

2-Chlorovinyl dichloro arsine (Lewisite gas)

(C_2) NAR in Aldehyde & Ketone : Due to strong electronegativity of oxygen, the mobile π electrons pulled strongly towards oxygen, leaving the carbon atom deficient of electrons. Carbon is thus readily attacked by Nu. The negatively charged oxygen is attacked by electron deficient (electrophile) E^+.



Reactivity	$\propto$	Magnitude of ∂+ve charge
of carbonyl group	$\propto$	– I effect
	$\propto$	$\dfrac{1}{+\text{I effect}}$

Illustrations

Illustration 1. Arrange the following for reactivity in decreasing order

(a) I. $H_2C=O$ II. $CH_3(H)C=O$ III. $(CH_3)_2C=O$

(b) I. $ClCH_2CHO$ II. NO_2CH_2CHO III. CH_3CHO IV. CH_3CH_2CHO

(c) I. CH_3CHO II. $ClCH_2CHO$ III. $HCCl_2CHO$ IV. CCl_3CHO

(d) I. $(CH_3)(CH_3)C=O$ II. $(CH_3CH_2)(CH_3)C=O$ III. $((CH_3)_2CH)(CH_3)C=O$ IV. $(CCl_3)(CH_3)C=O$

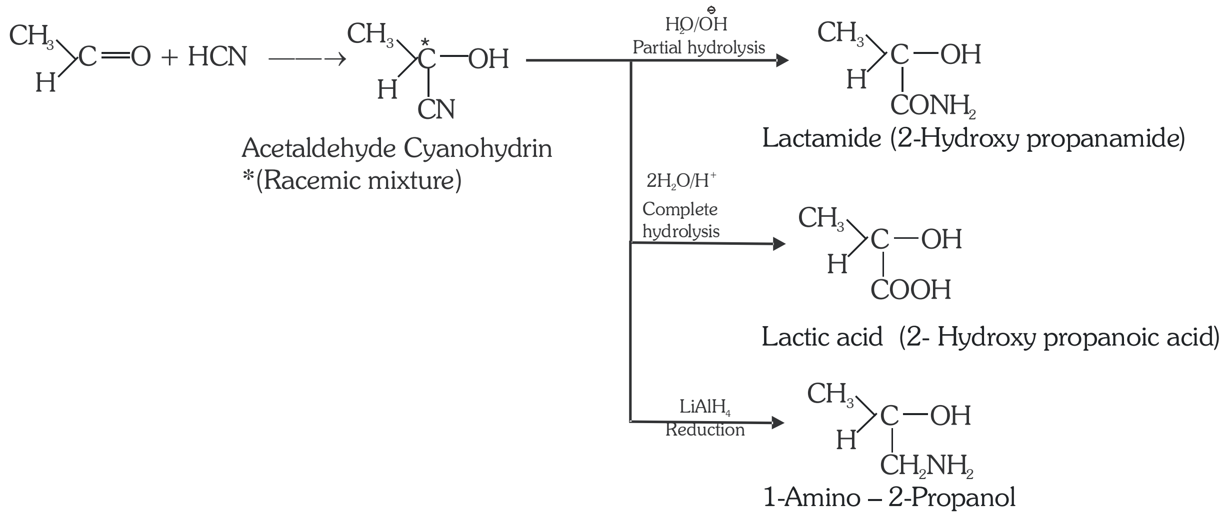
Solution. (a) I > II > III (b) II > I > III > IV

(c) IV > III > II > I (d) IV > I > II > III

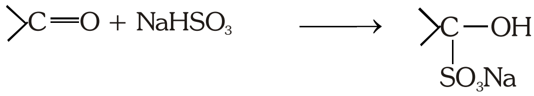
CH_3— is +I group, decreases the intensity of δ+ve charge on C-atom of $>C=O$ group.

Cl – is –I group increases the intensity of δ+ve charge on C-atom of $>C=O$ group.

(1) Addition of HCN :



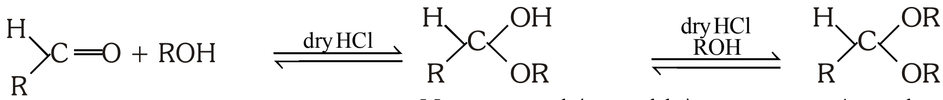
(2) Addition of $NaHSO_3$: This reaction is utilized for the separation of carbonyl compounds from non-carbonyl compounds.



Sodium bi sulphite

Bisulphite compound (White Crystalline)

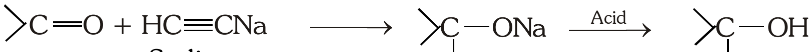
(3) With Alcohol :



Hemi-acetal (unstable)

Acetal

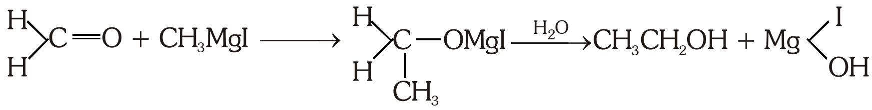
(4) Reaction with sodium alkynide :



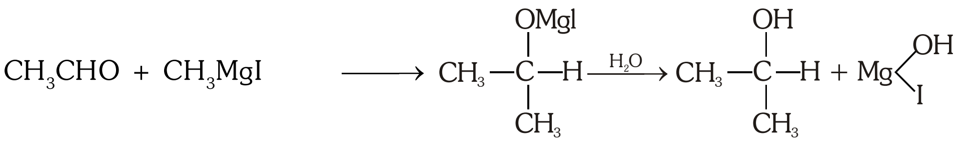
Sodium Alkynide

Acetylinic alcohol

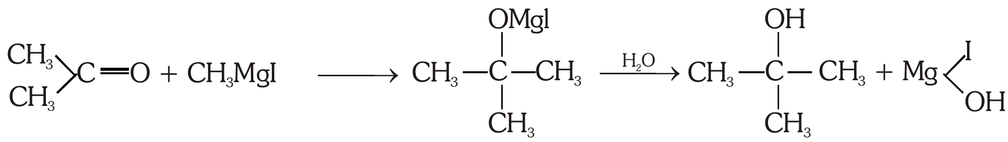
(5) Reaction with Grignard reagent :



Ethanol (1° alcohol)

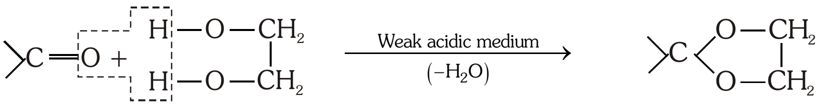


2–Propanol (2° alcohol)



2–Methyl–2–propanol (3° alcohol)

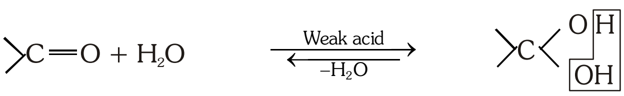
(6) Reaction with glycol :



(neutral)

Cyclic acetal / ketal

(7) Reaction with H_2O : It is a reversible reaction.



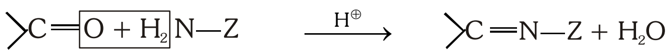
(neutral)

unstable hydrate

Note : Chloral ($Cl_3C–CH=O$) forms stable hydrate [CCl_3 – $CH(OH)_2$ (chloral hydrate)]

(8) Reaction with ammonia derivatives : These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.

$NH_3 \longrightarrow NH_2Z$ (Ammonia derivative)



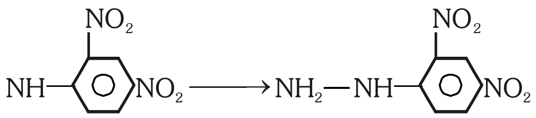
Addition - elimination (Condensation)

Ammonia derivatives (NH_2Z) :

Z = OH $\longrightarrow$ NH_2OH (Hydroxyl amine)

Z = NH_2 $\longrightarrow$ NH_2NH_2 (hydrazine)

Z = NHC_6H_5 $\longrightarrow$ $NH_2NHC_6H_5$ (Phenyl hydrazine)

Z = 

2, 4–Dinitro phenyl hydrazine (2,4-DNP) Brady's reagent.

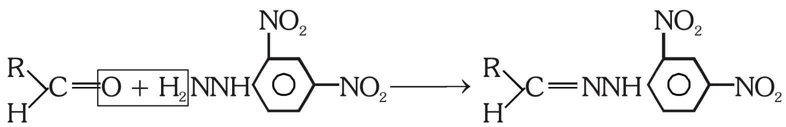
Z = $NHCONH_2$ $\longrightarrow$ $NH_2NHCONH_2$

Semi Carbazide.

$\begin{matrix}R\\H\end{matrix}\!>C=\boxed{O+H_2}NOH \longrightarrow \begin{matrix}R\\H\end{matrix}\!>C=NOH$ (Aldoxime)

$\begin{matrix}R\\H\end{matrix}\!>C=\boxed{O+H_2}NNH_2 \longrightarrow \begin{matrix}R\\H\end{matrix}\!>C=NNH_2$ (Hydrazone)

$\begin{matrix}R\\H\end{matrix}\!>C=\boxed{O+H_2}NNHC_6H_5 \longrightarrow \begin{matrix}R\\H\end{matrix}\!>C=NNHC_6H_5$ (Phenyl hydrazone)



(2, 4 - dinitro phenyl hydrazone) (Red organge ppt.)

$\begin{matrix}R\\H\end{matrix}\!>C=\boxed{O+H_2}NNHCONH_2 \longrightarrow \begin{matrix}R\\H\end{matrix}\!>C=NNHCONH_2$ (Semi Carbazone)

BEGINNER'S BOX-3

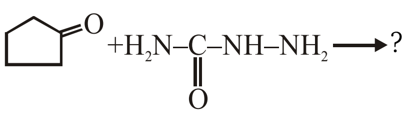
1. Which compound form more stable hydrate with H_2O?

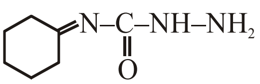
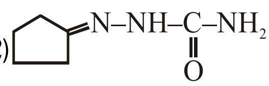
(1) CCl_3CHO (2) CH_3CHO (3) CH_3COCH_3 (4) $CH_3COC_2H_5$

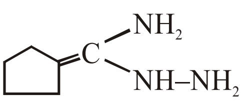
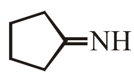
2. The formation of cyanohydrin from a ketone is an example of :-

(1) Electrophilic addition (2) Nucleophilic addition

(3) Nucleophilic substitution (4) Electrophilic substitution

3. 

(1)  (2) 

(3)  (4) 

4. $Ph-C\equiv C-CH_3 \xrightarrow[H_2SO_4]{HgSO_4} A$, A is

(1) $Ph-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$ (2) $Ph-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$ (3) $Ph-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ (4) $Ph-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

4.2 SUBSTITUTION REACTIONS :

Reactions in which one atom or a group of substrate is replaced by other atom or group are called as substitution reactions.

On the basis of reaction conditions and attacking species, substitution reaction is also of three types :

(A) Free radical substitution reactions

(B) Electrophilic substitution reactions

(C) Nucleophilic substitution reactions

(A) Free radical substitution reactions : Substitution reaction in alkanes show free radical mechanism.

They give following substitution reaction.

(a) Halogenation : Replacement of H-atom by halogen atom

$$R{-}H + X_2 \longrightarrow R{-}X + HX$$

Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temp.

The reactivity order for halogens shows the order.

$$\boxed{F_2 > Cl_2 > Br_2 > I_2}$$

Reactivity order of hydrogen atom in alkane is

$$\boxed{\text{Tertiary C} - \text{H} > \text{Sec. C} - \text{H} > \text{primary C} - \text{H}}$$

(i) **Fluorination :** Reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F_2 diluted with an inert gas like N_2.

(ii) **Chlorination :**

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

The monochloro derivative of alkane is obtained as major product by taking alkane in large excess.

When chlorine is in excess then perchloro derivative is obtained as major product.

$$\boxed{\text{At 12 noon explosively } CH_4 + Cl_2 \longrightarrow C + HCl}$$

Mechanism for $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$

Step I **Chain initiation step :** $Cl:Cl \xrightarrow[\text{or } \Delta]{UV} Cl^{\bullet} + Cl^{\bullet}$

Step II **Chain propagation step :** $Cl^{\cdot} + H:CH_3 \longrightarrow H:Cl + {}^{\cdot}CH_3$

Methane Methyl radical

$$\dot{C}H_3 + Cl:Cl \longrightarrow CH_3Cl + \dot{C}l$$

Step III **Chain termination step :** $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$, $CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow CH_3Cl$,

$$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$$

(iii) **Bromination** : Br_2 reacts with alkanes in a similar manner but less vigorously.

(iv) **Iodination :** Iodine reacts with alkanes reversibly. HI formed as the by product is a powerful reducing agent and is capable of reducing the CH_3I to CH_4.

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HNO_3, HgO etc. which decompose HI,

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Iodination is very slow because energy of activation of the reaction is very large

$$CH_4 + I^{\bullet} \longrightarrow HI + \dot{C}H_3$$

(b) Nitration : (Vapour phase nitration) This involves the substitution of a hydrogen atom of alkane with $-NO_2$ group.

At ordinary temperature, alkanes do not react with HNO_3. But reacts with vapours of Conc. HNO_3 at 450° C and in pressure.

$$R-H + HO-NO_2 \xrightarrow[\text{pressure}]{400-500^\circ C} R-NO_2 + H_2O$$

Since the reaction is carried at high temperature and in pressure, so the C—C bonds of alkanes also break during the reaction and a mixture of nitroalkanes is formed.

Ex. $CH_3-CH_3 + HNO_3 \xrightarrow{450^\circ C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$

$CH_3CH_2CH_3 + HNO_3 \xrightarrow{450^\circ C}$
- 1–Nitro propane
- 2–Nitro propane (major)
- Nitro ethane
- Nitromethane

(c) Sulphonation : Replacement of H atom of alkane by $-SO_3H$ is known sulphonation.

Alkane react with fuming H_2SO_4 or oleum ($H_2S_2O_7$).

Ex. $$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H + HO-SO_3H \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-SO_3H + H_2O$$

2–Methyl propane

The reactivity order for sulphonation is tert. H > Sec. H > prim. H

Note : The reaction is observed in higher alkanes and the alkanes having 3° H.

(d) Chlorosulphonation (Reed reaction) : Reaction with a mixture of SO_2 and Cl_2 at ordinary temp. in the presence of UV light is called chlorosulphonation.

$$C_3H_8 + SO_2 + Cl_2 \xrightarrow{UV} C_3H_7SO_2Cl + HCl$$

Propane sulphonyl Chloride

GOLDEN KEY POINTS

Allylic or benzylic substitution by Br_2 (low concentration)/hν or NBS/hν

$$CH_3-CH=CH_2 \xrightarrow[h\nu]{Br_2} \underset{\displaystyle Br}{\underset{|}{CH_2}}-CH=CH_2 + HBr$$

Mechanism :

I Chain initiation step :

$$Br_2 \xrightarrow{h\nu} \dot{B}r + \dot{B}r$$

II Chain propagation step :

$$CH_3-CH=CH_2 + \dot{B}r \longrightarrow \dot{C}H_2-CH=CH_2 + HBr$$

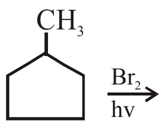
(stable by resonance)

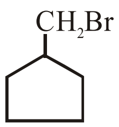
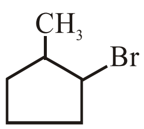
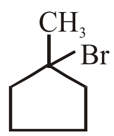
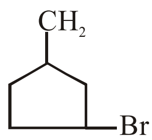
$$\dot{C}H_2-CH=CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}}-CH=CH_2 + \dot{B}r$$

(Product)

BEGINNER'S BOX-4

1. In the following reaction, the major product is :-



(1)  (2)  (3)  (4) 

2. The bond dissociation energy at the C–H bond for the compound :-

(I) CH_3H (II) $CH_3–CH_2–H$ (III) $CH_2=CH–CH_2–H$ (IV) $C_6H_5–H$

(1) I > II > III > IV (2) IV > III > II > I

(3) IV > I > II > III (4) II > I > IV > III

3. Arrange the following in correct order of reactivity towards $Cl_2/h\upsilon$ –

(A) CH_4 (B) CH_3CH_3 (C) $CH_3CH_2CH_3$ (D) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$

(1) A > B > C > D (2) D > C > B > A (3) B > C > A > D (4) C > B > D > A

4. Which of the following are free radical reactions:-

(a) $CH_3CH = CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2–Br$

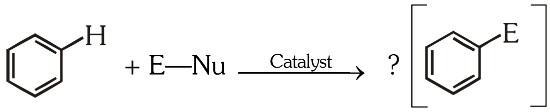
(b) $CH_3CH = CH_2 + HCl \xrightarrow{\text{peroxide}} CH_3CH(Cl)CH_3$

(c) $CH_3CH = CH_2 + Cl_2 \xrightarrow{500°C} Cl–CH_2CH=CH_2$

(d) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2Cl$

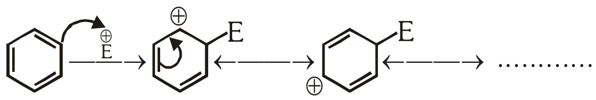
(1) Only d (2) a, c (3) a, b, d (4) a, c, d

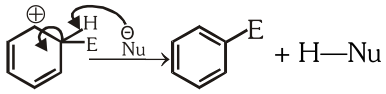
(B) Electrophilic substitution reaction [ESR] : Characteristic reaction of arenes is ESR



Mechanism :

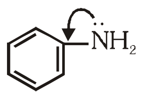
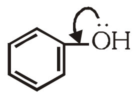
Formation of $\overset{\oplus}{E}$ $E - Nu \xrightarrow{\text{Catalyst}} \overset{\oplus}{E} + \overset{\ominus}{Nu}$

Attack of $\overset{\oplus}{E}$ 

Abstraction of $\overset{\oplus}{H}$ 

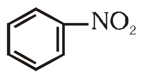
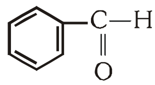
Illustrations

Illustration 2. Give reactivity order for electrophilic substitution reaction.

(i)  > 

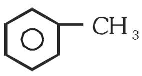
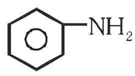
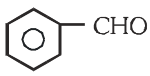
less EN of nitrogen so more +M so more e^- density so more reactive

less +M of –OH due to more EN

(ii)  < 

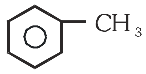
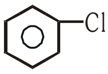
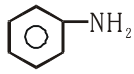
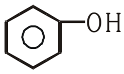
More –M of $–NO_2$ & more –I so e^- density decrease (more) so less reactive

less –M of –CHO & less –I so e^- density decreases (less) so more reactive.

(iii)    

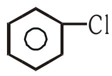
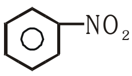
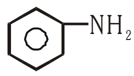
+H ↑   +M ↑   –M ↓

ESR order III > II > I > IV

(iv)    

+H ↑   –I > +M ↓   more +M due to less EN ↑   less +M ↑

ESR order III > IV > I > II

(v)    

– I   – M   + M

ESR order III > IV > I > II

(vi) 

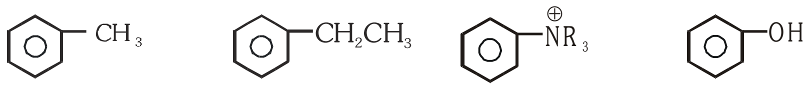
–H +H +M – M

ESR order III > II > I > IV

(vii) 

+M –M (more) –I –M (less)

ESR order I > III > IV > II

(viii) 

+H(more) +H (less) –I +M

ESR order IV > I > II > III

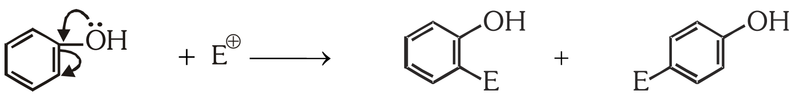
Note:

(1) ***ortho/para directing group or activating group :*** Group which direct electrophile on ortho and para position is called as o/p directing group.

These group increases electron density or increases reactivity of benzene ring so are called activating group.

These groups are :

$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}HCOCH_3$, $-\ddot{S}H$, $-\ddot{O}COR$, $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$



o— p—

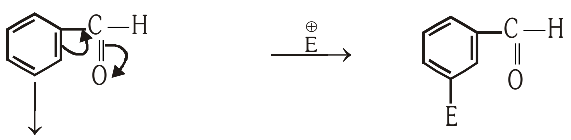
due to +M/+H of these groups electron density at ortho and para position is increased so electrophile easily attack on ortho/para position.

(2) ***Meta directing or deactivating group :*** Due to –M/–H of groups electron density at ortho and para position is less but more at meta position so electrophile attack on meta position. So, groups which direct electrophile on meta position are called as meta directing groups.

These groups decrease electron density in benzene ring and decrease reactivity of benzene ring so are called as deactivating group.

These groups are :

$-CHO$, $COOH$, $-COOR$, $-COR$, $-CN$, $-NO_2$, $-SO_3H$, $-CX_3$

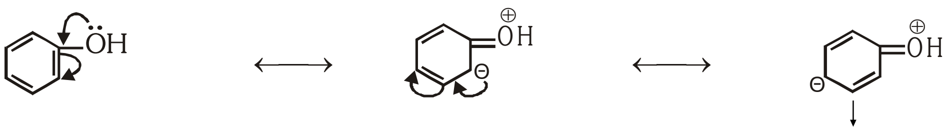


More e^- density at meta position

(3) Halogens are o/p directing group due to +M effect but are deactivating group due to –I > +M.

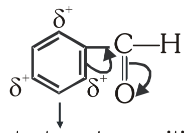
(4) M and H effect does not depend on distance while I–effect depends on distance In given example

(5) M-effect at meta position is considered zero.



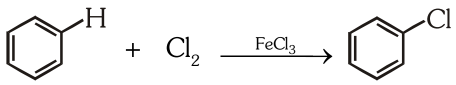
no effect at meta position

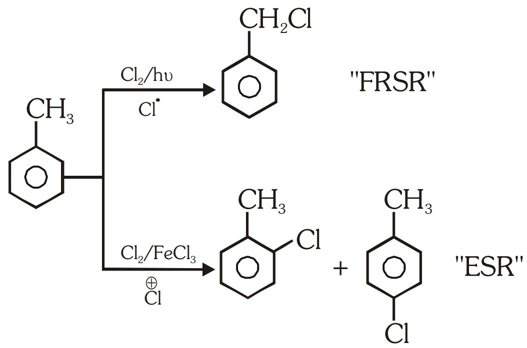
Similarly :



no effect at meta position

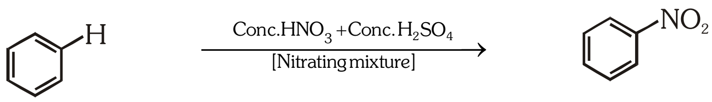
(i) Halogenation :





Note: CH_3 group in toluene is o/p directing and activating group.

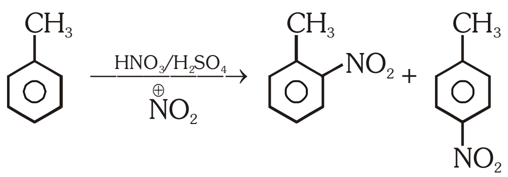
(ii) Nitration :



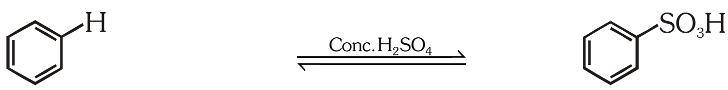
Formation of $\overset{\oplus}{E}$

$$H\ddot{O}-NO_2 + \overset{+\delta}{H}-\overset{-\delta}{HSO_4} \longrightarrow H_2\overset{\oplus}{O}-NO_2 + \overset{\ominus}{HSO_4} \xrightarrow{-H_2O} \overset{\oplus}{NO_2}$$

(Bronsted base) (Bronsted acid) [Attacking species]

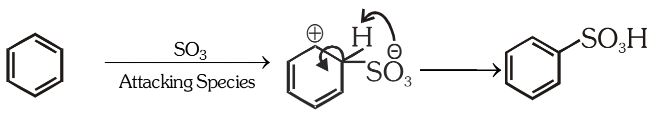


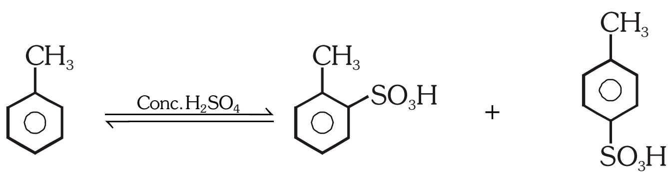
(iii) Sulphonation :



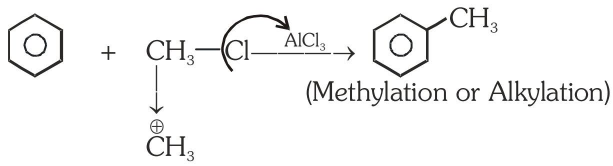
Mechanism :

$$2H_2SO_4 \rightleftharpoons SO_3 + \overset{\ominus}{HSO_4} + H_3\overset{\oplus}{O}$$

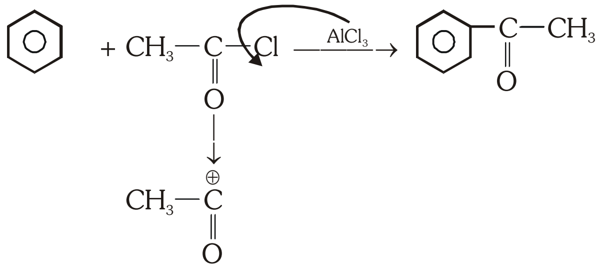




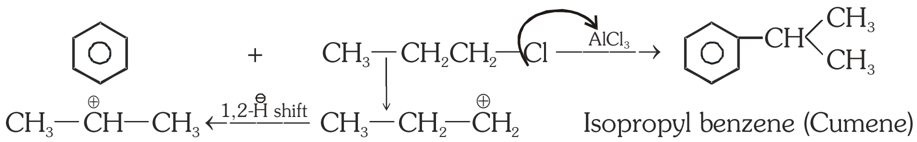
(iv) Friedel crafts reaction [FCR] : Alkylation or acylation of arenes in presence of lewis acid [$FeCl_3$, $AlCl_3$ or $ZnCl_2$...] is called as FCR.



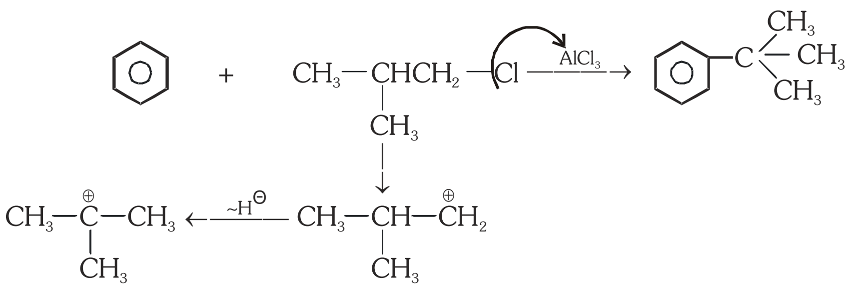
(Methylation or Alkylation)

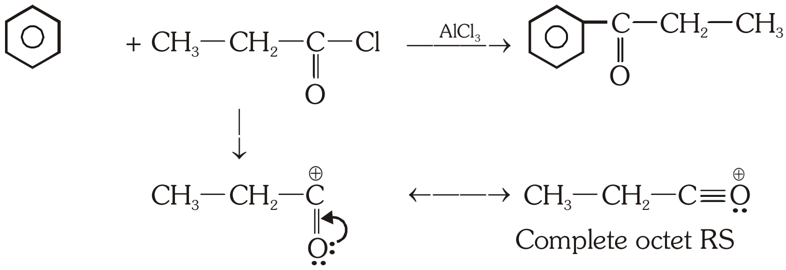


Intermediate carbocation is formed in FCR so rearrangement is possible.

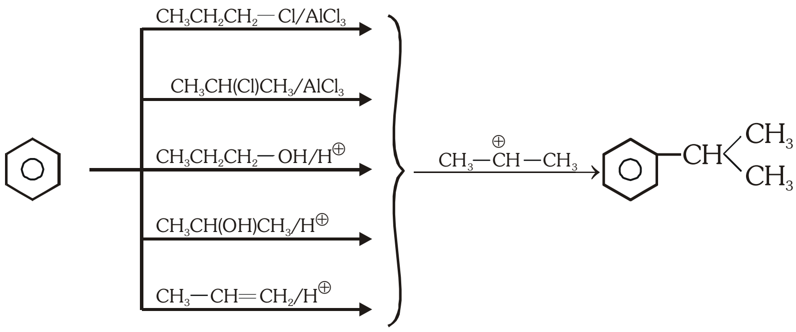


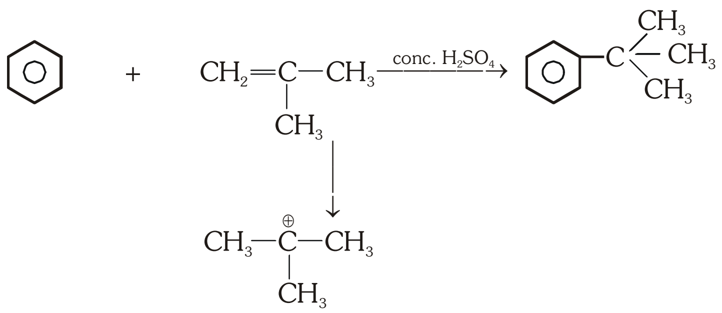
Isopropyl benzene (Cumene)

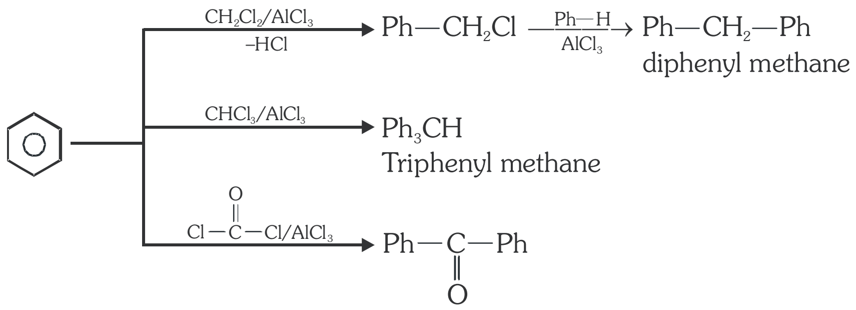




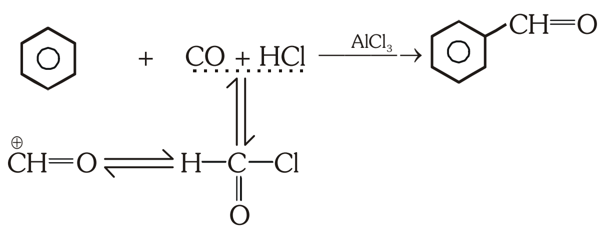
Complete octet RS



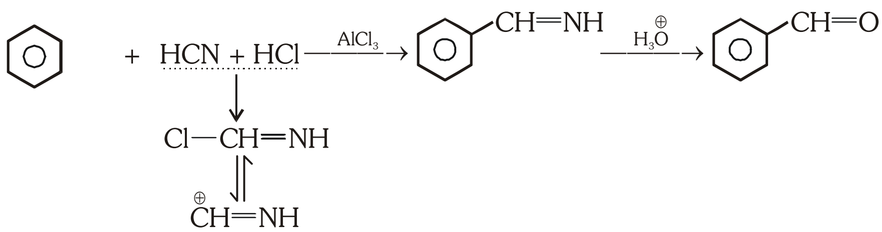




(vi) Gatterman's Koch Reaction :



(vii) Gatterman's Aldehyde synthesis :



GOLDEN KEY POINTS

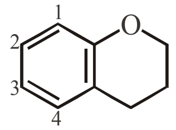
The important electrophiles used in the aromatic substitution are the following -

Electrophilic	Source	Name of substitution reaction
Cl^+ (Chloronium)	$Cl_2 + AlCl_3$ or $FeCl_3$	Chlorination
Br^+ (Bromonium)	$Br_2 + AlBr_3$ or $FeBr_3$	Bromination
NO_2^+ (Nitronium)	(conc. HNO_3 + H_2SO_4)	Nitration
SO_3 (Sulphertrioxide)	conc. H_2SO_4, fuming sulphuric acid	Sulphonation
R^+ (Alkyl carbonium)	$RX + AlX_3$ (X= Cl or Br) $ROH + H^+$	Friedel crafts (Alkylation)
$R-\overset{\oplus}{C}=O$ (Acyl carbonium)	$RCOCl + AlCl_3$	Friedel crafts (Acylation)

BEGINNER'S BOX-5

1. Which of the following group is ortho para director :-

(1) $-NH-\overset{\overset{O}{\|}}{C}-CH_3$ (2) $-\overset{\overset{O}{\|}}{C}-NH_2$ (3) $-C\equiv N$ (4) $-\overset{\overset{O}{\|}}{C}-OCH_3$

2.  $\xrightarrow[Fe]{Br_2}$ Substitution takes place at the position.

(1) 1 (2) 2 (3) 3 (4) Both (1) and (3)

(C) Nucleophilic substitution reaction (S_N) : Due to electronegativity difference the $-\overset{|}{\underset{|}{C}}-X$ bond is polarised bond. $\left(-\overset{|\delta+}{\underset{|}{C}}-\overset{\delta-}{X}\right)$

Thus the C-atom of the $\overset{\delta+}{C}-\overset{\delta-}{X}$ bond becomes centre to attack by a nucleophile $(\overset{\ominus}{Nu})$.

$X^{\ominus}$ ion from R—X molecule is substituted by a $\overset{\ominus}{Nu}$. i.e.S_N reaction are the most common reactions in R—X.

$$R—X + \overset{\ominus}{Nu} \longrightarrow R—Nu + X^{\ominus}$$

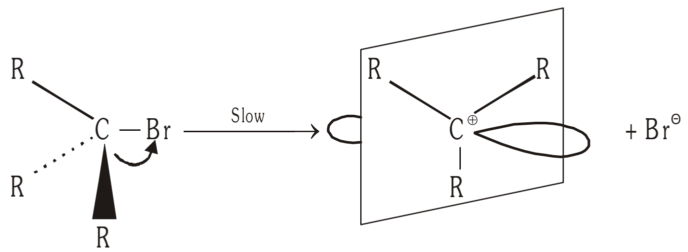
Two mechanisms are observed in S_N reaction :

(a) S_N1 mechanism (b) S_N2 mechanism

Mechanism of S_N1 and S_N2 :

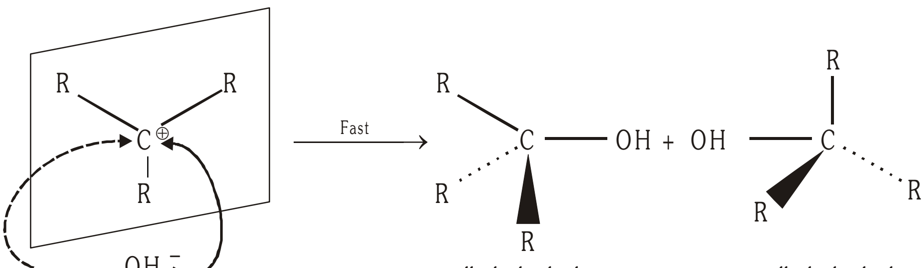
S_N1 ***Mechanism*** : S_N1 stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionises to give a planar corbonium ion. The corbonium ion is planar because the central positively charged carbon is sp^2 hybridized.



t-alkyl bromide

Step-2 : The nucleophile can attack the planar carbonium ion from either side to give the product.



t-alkyl alcohol t-alkyl alcohol

(i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed depends upon the concentration of tertiary alkyl halide alone.

$\therefore$ Rate = K[R_3C—Br]

It is obvious that the reaction follows first order kinetics, therefore reaction is called S_N1.

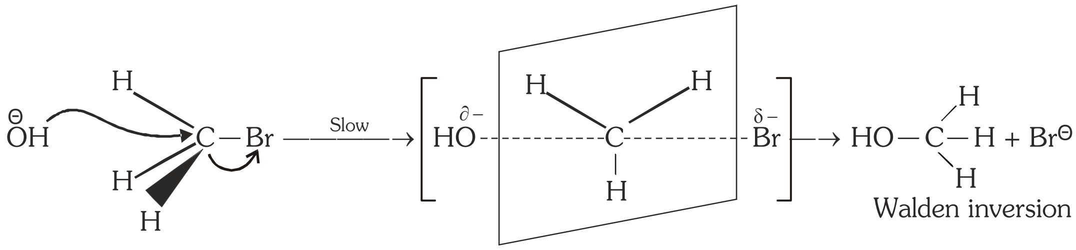
(ii) The reactivity order for S_N1 reaction $\propto$ stability of carbocations formed by halides.

$\therefore$ reactivity order of halides (S_N1) varies as follows :

Benzyl halide > Allyl 3°halide > Allyl 2° halide > Allyl 1° halide > 3°halide > 2° halide > 1° halide > methyl halide.

(iii) Remember that in case alkyl halide is optically active, S_N1 reactions lead to racemisation.

S_N2 mechanism : S_N2 stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, bond making and bond breaking process occur simultaneously.



Transition state

(i) Reactivity of alkyl halides in S_N2 substitution is governed by steric factors. The bulkier the group, that less reactive it will be.

(ii) Reactivity order of alkyl halide varies as follows :

allyl halide > CH_3X > 1°halide > 2°halide > 3° halide

(iii) The order of reactivity among 1° alkyl halides is : ***CH_3X > C_2H_5X > C_3H_7X*** etc.

Remember that in case alkyl halide is optically active, S_N1 reactions lead to Walden inversion.

(iv) For a given alkyl group the order of reactivity is - (for S_N1 and S_N2 both) : ***RI > RBr > RCl > RF***

(v) In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β–elimination it may proceed by E^1 or E^2 mechanism (analogous to S_N1 and S_N2 mechanism).

The order of elimination reaction is : ***3° halides > 2° halides > 1° halides***

(1) nucleophilic substitution reaction (S_N) in alkyl halide :

	Replacement of	Product
(a)	R—X $\xrightarrow{\text{HOH(Warm)}}$	R—OH (alcohol) + HX
(b)	R—X $\xrightarrow{\text{KOH aq. }\Delta}$	R—OH (alcohol) + KX
(c)	R—X $\xrightarrow{\text{moist }AgO_2}$	R—OH (alcohol) + AgX
(d)	R—X $\xrightarrow{\text{KSH alc. }\Delta}$	R—SH + KX Alkane thiol (Mercaptane)
(e)	R—X $\xrightarrow{\text{NaSR'}}$	RSR' + NaX Thioether
(f)	R—X $\xrightarrow{\text{R' COOAg }\Delta}$	R' COOR + AgX (Alkyl alkanoate) ester

(g) Reaction with KCN and AgCN :

$$\overset{\delta+}{R}-\overset{\delta-}{X} + \overset{+}{K}\overset{-}{CN} \xrightarrow[\Delta]{\text{Alc.}} R-C\equiv N + KX$$

Ionic bond — cyanide (major)

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Ag-C\ddot{N} \xrightarrow[\Delta]{\text{Alc.}} R-N\overset{\rightarrow}{=}C + Ag-X$$

covalent bond — isocyanide (major)

(h) Reaction with KNO_2 and $AgNO_2$:

$$\overset{\delta+}{R}-\overset{\delta-}{X} + \overset{+}{K}\,\overset{-}{O}-N=O \xrightarrow[\Delta]{\text{Alc.}} R-O-N=O + KX$$

Ionic bond — (Alkyl nitrites) (major)

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Ag-O-\ddot{N}=O \xrightarrow[\Delta]{\text{Alc.}} R-N\overset{\nearrow O}{\underset{\searrow O}{}} + Ag-X$$

covalent bond — Nitroalkane (major)

(i) Reaction with NaOR' (Sodium alkoxide) :

$$R-X + NaOR' \longrightarrow R-OR' + NaX$$

(williamson ether synthesis reaction)

Ex. (i) $CH_3-CH_2-Cl + NaOCH_3 \longrightarrow CH_3-CH_2-O-CH_3$

(ii)
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + NaOCH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaCl + CH_3OH$$

more reactive towards elimination — (Alkene)

(j) Reaction with NH_3:

Ex. (i)
$$R-X + NH_3 \longrightarrow R-NH_2 \xrightarrow{R-X} R-NH-R \xrightarrow{R-X} R-\underset{\underset{R}{|}}{N}-R \xrightarrow{R-X} \left[R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{\overset{\oplus}{N}}}-R\right] X^{\ominus} \text{ (Quaternery salt)}$$

(ii) $R-X + \underset{\text{(excess)}}{NH_3} \longrightarrow \underset{\text{(Major)}}{R-NH_2} + H-X$

(iii) $\underset{\text{(excess)}}{R-X} + NH_3 \longrightarrow R_4\overset{\oplus}{N}\overset{\ominus}{X}$ (major)

(iv) $CH_3—CH_2—Cl + NH_3 \longrightarrow CH_3—CH_2—NH_2 + HCl$

(v) $CH_3—\underset{\displaystyle |\atop \displaystyle Cl}{CH}—CH_3 + NH_3 \longrightarrow CH_3—\underset{\displaystyle |\atop \displaystyle NH_2}{CH}—CH_3 + HCl$

(vi) $CH_3—\overset{\displaystyle CH_3\atop \displaystyle |}{\underset{\displaystyle |\atop \displaystyle CH_3}{C}}—Cl + NH_3 \longrightarrow CH_3—\overset{\displaystyle CH_2\atop \displaystyle \|}{\underset{\displaystyle |\atop \displaystyle CH_3}{C}} + NH_4Cl$

more reactive towards elimination (Elimination is more)

(k) Reaction with $CH\equiv CNa$:

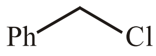
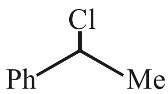
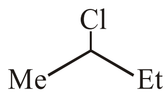
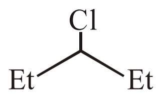
$R—X + CH\equiv CNa \xrightarrow{\Delta} R—C\equiv CH + NaX$

If $CH_3—\overset{\displaystyle CH_3\atop \displaystyle |}{\underset{\displaystyle |\atop \displaystyle CH_3}{C}}—X + CH\equiv \overset{-}{C}\overset{+}{Na} \xrightarrow{\Delta} CH_3—\underset{\displaystyle |\atop \displaystyle CH_3}{C}=CH_2 + NaX + CH\equiv CH$

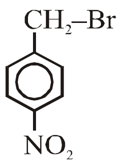
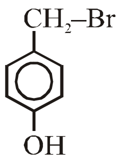
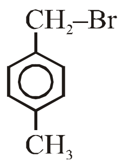
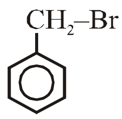
(Elimination is more)

BEGINNER'S BOX-6

1. Which is most reactive for S_N1 reaction :-

(1) 
(2) 
(3) 
(4) 

2. Which is most reactive for SN^1?

(1) 
(2) 
(3) 
(4) 

NSR reaction of alcohol :-

(a) Reaction with HX :

eg. $R—CH_2—OH \xrightarrow[\text{anhy. } ZnCl_2]{H–X} RCH_2—X$

Mechanism :

$$R—CH_2—\ddot{O}H \xrightarrow[(H—X)]{H^+} R—CH_2—\underset{\displaystyle |\atop \displaystyle H}{\overset{\oplus}{O}}—H \xrightarrow{-H_2O} R—\overset{\oplus}{C}H_2 \xrightarrow{X^{\ominus}} R—CH_2—X$$

(Unstable) (Product)

In this reaction, intermediate carbocation is formed so rearrangement can take place.

anhy. $ZnCl_2$ act as dehydrating agent and absorbs H_2O from the reaction so good yield of halide is obtained. Also it generates H^+ from HCl.

$$HCl + ZnCl_2 \longrightarrow ZnCl_3^{\ominus} + H^{\oplus}$$

Reactivity order for alcohol :

$\boxed{\text{Reactivity} \propto \text{stability of intermediate carbocation}}$, so reactivity order : **Tert. alc. > Sec. alc. > Pri. alc.**

Reactivity order of H—X is : **HI > HBr > HCl**

HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.

$$R—OH + HI \longrightarrow R—I + H_2O$$

HCl and also 1° alcohol are less reactive so $ZnCl_2$ or some amount of H_2SO_4 is needed to increase the reactivity.

eg. $$CH_3—CH_2—OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3—CH_2—Cl$$

At normal condition :

$$CH_3—CH_2—OH + HCl \longrightarrow \times \text{(no reaction)}$$

Note : $[HCl_{(conc.)} + ZnCl_{2\,(anhydrous)}]$ is called as **lucas reagent,** alcohol gives turbidity with lucas reagent.

Reactivity towards lucas reagent (difference in 1°, 2° and 3° alcohol).

	1° alcohol	2° alcohol	3° alcohol
Time to give turbidity	in 30 min. on heating	in 5 min.	in 2-3 second

(b) Reaction with phosphorus halides :

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

$$3R—OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

PBr_3 and PI_3 are less stable, thus for bromides and Iodides, $(P + Br_2)$ Or $(P + I_2)$ mixture is used.

(c) Reaction with thionyl chloride - (Darzen's procedure) :

$$\underset{\text{One mole}}{R—OH} + \underset{\text{One mole}}{SOCl_2} \xrightarrow[\text{(1 mole)}]{\text{Pyridine}} R—Cl + SO_2 + HCl$$

NSR reaction in ether :-

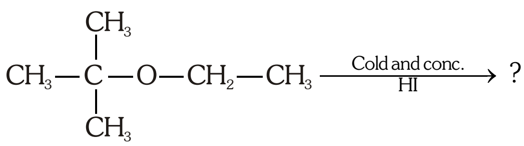
Reaction with HX : Reactivity of HX $\boxed{\textbf{HI>HBr>HCl}}$

(A) Reaction with cold conc. HX : Ethers forms oxonium salt with cold and conc. HCl (less reactive) Cold conc. HI and HBr (more reactive) break C–O bond.

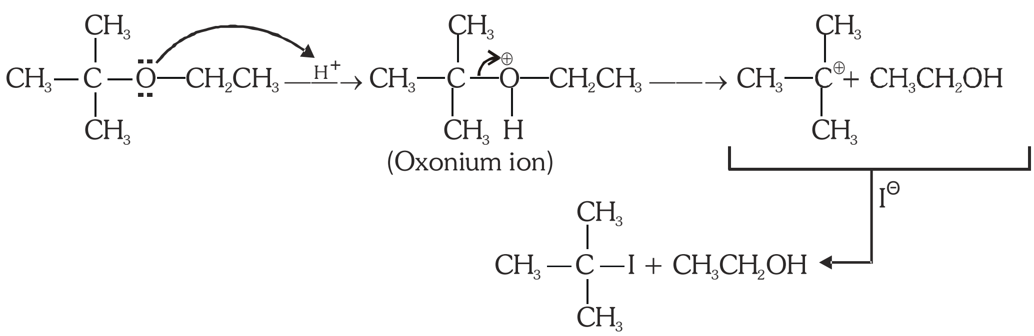
(B) Reaction with conc. HI or conc. HBr :

$$CH_3CH_2—O—CH_3 \xrightarrow{\text{hot and conc HI}} CH_3CH_2—I + CH_3—I$$

Illustrations

Illustration 3. 

Solution. **Mechanism**



If oxonium ion gives more stable carbocation [$Ph\overset{\oplus}{C}H_2$, $CH_2{=}CH{-}\overset{\oplus}{C}H_2$, $(CH_3)_3\overset{\oplus}{C}$] then SN^1 reaction occurs.

If oxonium ion gives less stable carbocation [$P\overset{\oplus}{h}$, $CH_2{=}\overset{\oplus}{C}H$, $CH_3\overset{\oplus}{C}H_2$, $(CH_3)_2\overset{\oplus}{C}H$] then SN^2 reaction occurs, and $X^{\ominus}$ attacks at less hindered carbon

Illustration 4. $CH_3CH_2{-}O{-}CH_2Ph \xrightarrow[HI]{\text{Cold conc.}} CH_3CH_2{-}OH + PhCH_2{-}I$, write mechanism of given reaction.

Solution. **Mechanism :** $CH_3CH_2\ddot{O}CH_2Ph \xrightarrow{H^{\oplus}} CH_3CH_2{-}\overset{\oplus}{O}(H){-}CH_2Ph$

$$CH_3CH_2OH + Ph\overset{\oplus}{C}H_2 \xrightarrow{I^{\ominus}} PhCH_2I + CH_3CH_2{-}OH \qquad (S_N1)$$

Illustration 5. $CH_3CH_2{-}O{-}CH_3 \xrightarrow{\text{conc. and cold HI}} ?$

Solution. $CH_3CH_2{-}\ddot{O}{-}CH_3 + \xrightarrow{H^+} CH_3CH_2{-}\overset{\oplus}{O}(H){-}CH_3 \xrightarrow{I^{\ominus}} CH_3I + CH_3CH_2OH \qquad (S_N2)$

Oxonium ion gives less stable carbocation

SN^2 reaction $I^{\ominus}$ attacks at less hinderd carbon.

Illustration 6. $CH_3{-}CH_2{-}O{-}Ph \xrightarrow[HBr]{\text{cold and conc.}} ?$

Solution. **Mechanism :**

$$CH_3{-}CH_2{-}\ddot{O}{-}Ph \xrightarrow{H^+} CH_3{-}CH_2{-}\overset{\oplus}{O}(H){-}Ph \xrightarrow{Br^{\ominus}} CH_3CH_2Br + PhOH$$

Note : If excess of HI/Δ is used then two moles of alkyl hallides are formed.

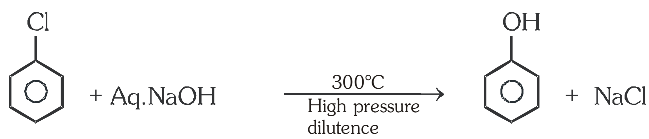
$$CH_3CH_2{-}O{-}CH_2Ph \xrightarrow[\Delta]{HI} CH_3CH_2OH + PhCH_2I \xrightarrow[\Delta]{HI} CH_3CH_2-I + PhCH_2-I$$

Illustration 7. $C_2H_5{-}O{-}C_2H_5 \xrightarrow{\text{hot and conc. HBr}} ? + ?$

Solution. $C_2H_5{-}Br + C_2H_5{-}Br$

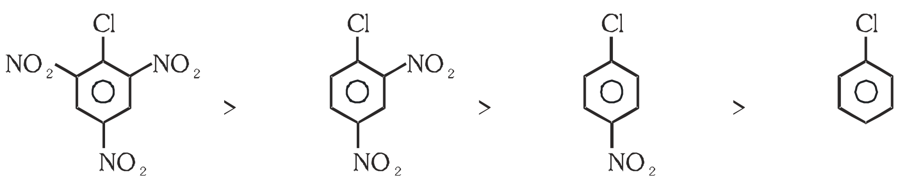
Aromatic nucleophilic substitution :

NSR reaction in halobenzene :-



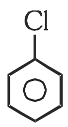
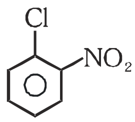
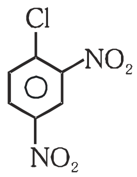
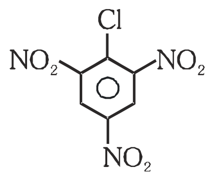
Presence of deactivating group at ortho and para position makes the nucleophilic substitution easier.

Reactivity Order : (Towards nucleophilic substatitution)



Illustrations

Illustration Which of the following undergoes Hydrolysis most easily :

(1)  (2)  (3)  (4) 

Solution. If there is more e^- withdrawing groups then there will be more nuclephilic substitution reaction.

Ans. (4)

Illustration The product in the following reaction is :

$$Ph - Cl + Fe / Br_2 \longrightarrow \text{Product}$$

(1) o– bromo-chloro benzene (2) p– bromo-chloro benzene

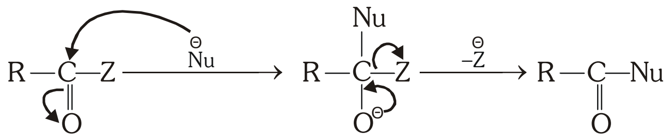
(3) (1) and (2) both (4) 2, 4, 6-tribromo chloro benzene

Solution. Since – Cl group is deactivating and o/p directing group so o– and p– products are formed.

Ans. (3)

NSR in Acid derrivatives :

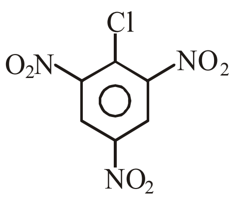
Example : Hydrolysis of acid derrivatives :

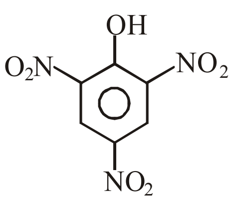
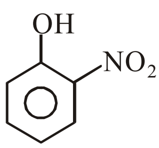
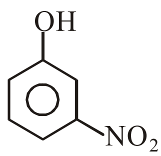


Where Z= —Cl, —OR, $—NH_2$, $—O—C(=O)—R$

here Z is a good leaving group

BEGINNER'S BOX-7

1.  $\xrightarrow[\Delta,\ \text{pressure}]{NaOH}$?

(1)  (2)  (3)  (4) 

2. Which one of the following is least reactive with water

(1) $CH_3-C(=O)-Cl$ (2) $C_6H_5-C(=O)-NH_2$

(3) $CH_3-C(=O)-NH_2$ (4) $C_6H_5-C(=O)-Cl$

3. $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\ominus\,\oplus}{O}Na + CH_3Cl \longrightarrow$

(1) $CH_3-\underset{\underset{CH_2}{\|}}{CH}$ (2) $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_3$

(3) $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_2-CH_3$ (4) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

4.3 ELIMINATION REACTIONS : These reactions are involve elimination of small molecule from the substrate

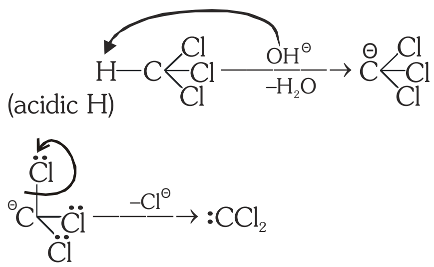
Elimination

- α–elimination or 1, 1–elimination
- β–elimination or 1, 2–elimination

α-Elimination (1, 1-Elimination) : Removal of H and X from one C-atom

Example : $CHCl_3 \xrightarrow{KOH}$: CCl_2 (dichloro carbene)

Mechanism :



α, β Elimination (β-elimination) : Removal of H and X from adjacent C-atoms

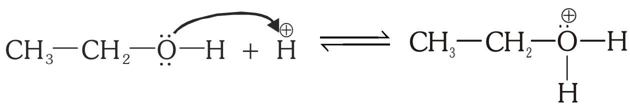
β — E_1 unimolecular elimination
  — E_2 bimolecular elimination

(a) Unimolecular elimination (E_1) :-

$$CH_3-CH_2-OH \xrightarrow[443^{\circ}K]{95\%\,H_2SO_4} CH_2=CH_2$$

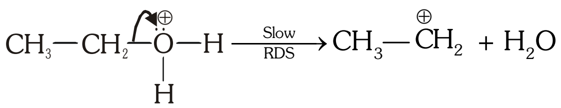
Mechanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows :

Step I : Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows:



Ethanol (From acid) Protonated ethanol

Step II : Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C – O bond becomes weak and cleaves as follows :



Ethyl carbocation

This is a slow and is regarded as **rate determining step in E_1 reaction.**

Step III : Base removes Hα (proton) from carbocation and changes it into ethene in a fast step as follows:

$$H{-}CH_2{-}\overset{\oplus}{C}H_2 \xrightarrow[\text{fast}]{\text{Base}} CH_2{=}CH_2$$

Ethene

> **Saytzeff rule :** When two possible alkenes are obtained by the elimination reaction then that alkene containing maximum number of alkyl group on double bonded C-atoms is called Saytzeff's product and formed as major product.

Note : The alkene having less number of alkyl groups on double bonded C-atoms is called Hofmann's product.

Example : (i) $CH_3{-}CH_2{-}\underset{}{\overset{OH}{\overset{|}{C}H}}{-}CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3{-}CH{=}CH{-}CH_3 + CH_3{-}CH_2{-}CH{=}CH_2$

2–butanol — main product 2–butene 80% (Saytzeff's product) — 1–butene 20% (Hoffmann's product)

(ii) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH \xrightarrow[\Delta]{H_2SO_4} CH_3{-}CH{=}CH{-}CH_3 + CH_3CH_2CH{=}CH_2$

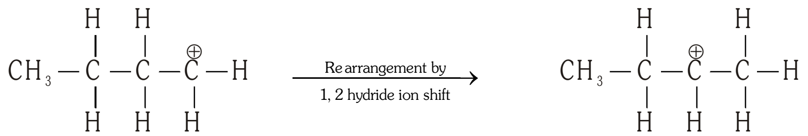
1–butanol — 2–butene80% Main product — 1–butene 20%

Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

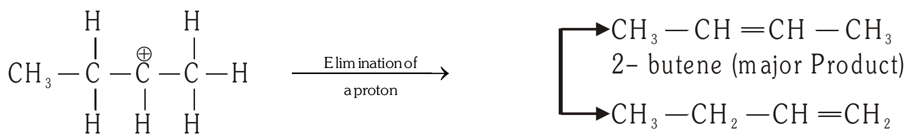
$$CH_3CH_2CH_2{-}CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + \overset{\oplus}{H} \longrightarrow CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2$$

$$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2 \longrightarrow CH_3CH_2CH_2{-}\overset{\oplus}{C}H_2 + H_2O$$

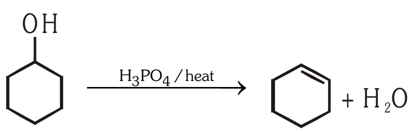
Primary Carbonium ion



1^0 Carbonium — 2^0 Carbonium more stable



1–butene (minor product)

(iii) 

Cyclohexanol — Cyclohexene

Reactivity order of acidic dehydration of alcohols is : 3° > 2° > 1° R–OH

- Rate of reaction ∝ [substrate]
- Molecularity of reaction = 1 (So reaction is called as E_1)
- In reaction intermediate carbocation is formed, so carbocation rearrangement is possible.

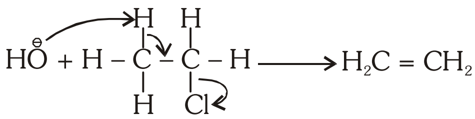
(b) Bimolecular elimination (E_2) :

Example :

(i) Dehydrohalogenation of halides by alcoholic KOH/$NaNH_2$:

$$CH_3\text{–}CH_2\text{–}Cl + KOH_{(alc.)} \longrightarrow CH_2 = CH_2 + KCl + H_2O$$

Mechanism :



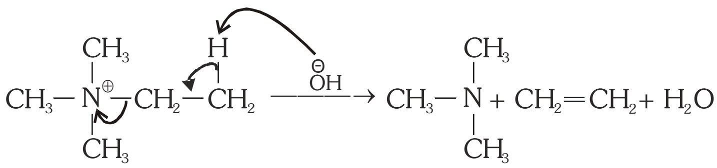
- Rate of reaction α [substrate] [base]
- Order of reaction = 2 (So reaction is E_2)
- In E_2 reaction intermediate (carbocation) is not formed. So there will be no carbocation rearrangement.

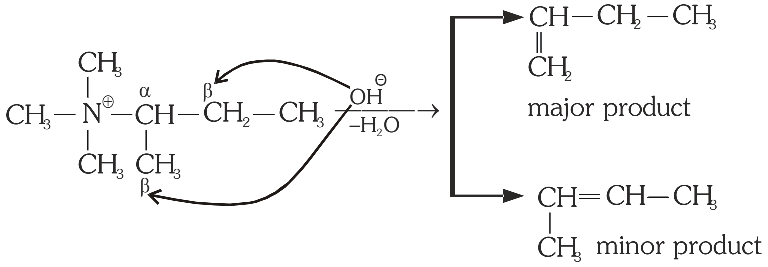
$$CH_3\text{—}\underset{\displaystyle Cl}{\underset{|}{C}H}\text{—}CH_3 \xrightarrow[\text{(KOH)}]{\text{Alc.}} CH_2{=}CH\text{—}CH_3$$

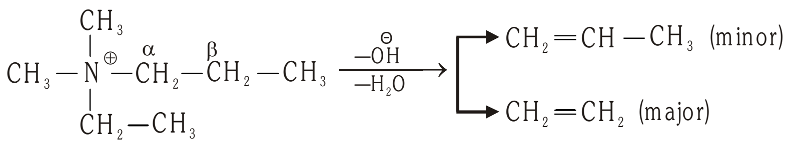
$$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}Cl \xrightarrow[\text{(KOH)}]{\text{Alc.}} CH_3\text{—}CH_2\text{—}CH{=}CH_2$$

$$CH_3\text{—}\underset{\displaystyle Cl}{\underset{|}{C}H}\text{—}CH_2\text{—}CH_3 \xrightarrow[\text{KOH}]{} \underset{\text{(major) (Saytzeff's product)}}{CH_3\text{—}CH{=}CH\text{—}CH_3} + \underset{\text{(minor) (Hoffmann's product)}}{CH_2{=}CH\text{—}CH_2\text{—}CH_3}$$

(ii) Pyrolysis of tetra alkyl ammonium ion :



Ex. 

Ex. 

Note : Hoffmann's product is formed as major product.

Competition between substitution and elemination reactions

Reactivity order of alkyl halides :

E_1- Reaction : 1° < 2° < $\boxed{3°}$

E_2- Reaction : 1° < 2° < $\boxed{3°}$

S_N1-Reaction : 1° < 2° < $\boxed{3°}$

S_N2-Reaction : $\boxed{1°}$ > 2° > 3°

GOLDEN KEY POINTS

- SN^2/E^2 is favoured by high conc. of good neucleophile or strong base. ($CH_3O^{\ominus}$, $HO^{\ominus}$)

  Rate of Reaction $\propto$ (Substrate) (Reagent)

- SN^1/E^1 is favoured by low conc. of poor neucleophile or weak base (CH_3OH, H_2O)

- If an alkyl halide, undergoes SN^2/SN^1 then SN^2 reaction will be favoured by high conc. of good neucleophile (negetively charged) in presence of polor aprotic solvent where as SN^1 – reaction is favoured by low conc. of poor neucleophile (neutral) in presence of polar protic solvent.

  Polar protic solvent : H_2O, CH_3OH, HCOOH

  Polar aprotic solvent : DMSO, CH_3CN, $C_2H_5–O–C_2H_5$, DMF

4.4 ISOMERIZATION REACTIONS : These reaction involves the interconversion of one isomer into the another isomer.

For example :

(i) $$CH_3-CH_2-CH_2-CH_3 \xrightarrow[+HCl,\ \Delta]{AlCl_3} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

(ii) $$CH_3-CH_2-CH=CH_2 \xrightarrow[H_2SO_4,\ \Delta]{Al_2(SO_4)_3} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + CH_3-CH=CH-CH_3$$

(iii) $$CH_3-CH_2-C\equiv CH \underset{NaNH_2}{\overset{Alc.KOH}{\rightleftharpoons}} CH_3-C\equiv C-CH_3$$

BEGINNER'S BOX-8

1. Acidic dehydration of alcohol involves :-

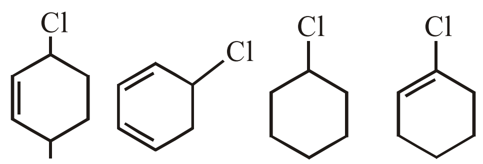
(1) E_1 elimination

(2) Carbocation rearrangement if possible

(3) Saytzeff's product is formed as major product

(4) All

2. Arrange the following in order of their reactivity toward dehydrohalogenation :-



I II III IV

(1) II > I > III > IV (2) III > II > I > IV

(3) IV > III > I > II (4) I > II > III > IV

REACTION AT A GLANCE :

S.N.	Class of compounds	Types of reactions
(i)	Alkane	Free radical substitution
(ii)	Alkene, alkyne	Electrophilic addition
(iii)	Alkyl halide	Nucleophilic substitution
(iv)	Aldehyde, ketone	Nucleophilic addition
(v)	Acid and their derivatives	Nucleophilic substitution
(vi)	Aromatic compounds	Electrophilic substitution

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3
	Ans.	1	1	3

BEGINNER'S BOX-2	Que.	1	2
	Ans.	3	1

BEGINNER'S BOX-3	Que.	1	2	3	4
	Ans.	1	2	2	2

BEGINNER'S BOX-4	Que.	1	2	3	4
	Ans.	3	3	2	4

BEGINNER'S BOX-5	Que.	1	2
	Ans.	1	4

BEGINNER'S BOX-6	Que.	1	2
	Ans.	2	2

BEGINNER'S BOX-7	Que.	1	2	3
	Ans.	1	2	2

BEGINNER'S BOX-8	Que.	1	2
	Ans.	4	1

EXERCISE-I (Conceptual Questions)

ELECTROPHILIC ADDITION REACTION

1. Correct reactivity order for EAR of following compounds is

$Ph—CH{=}CH_2$ (I) $\qquad$ $Ph—\underset{}{\overset{CH_3}{\overset{|}{C}}}{=}CH—CH_3$ (II)

$Ph_2C{=}CH—CH_3$ (III) $\qquad$ $CH_2{=}CH—NO_2$ (IV)

(1) IV > I > II > III $\qquad$ (2) III > II > I > IV

(3) II > III > I > IV $\qquad$ (4) II > III > IV > I

2. The intermediate during the addition of HCl to propene in the presence of peroxide is

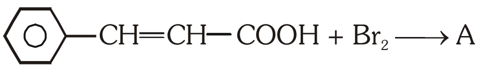
(1) $CH_3\dot{C}H\,CH_2Cl$ $\qquad$ (2) $CH_3\overset{\oplus}{C}H—CH_3$

(3) $CH_3—CH_2—\overset{\oplus}{C}H_2$ $\qquad$ (4) $CH_3\dot{C}HCH_3$

3. Hydroboration of isobutylene followed by oxidative alkaline hydrolysis gives

(1) 1–butanol $\qquad$ (2) 2–butanol

(3) Isobutyl alcohol $\qquad$ (4) $(CH_3)_3C–OH$

4. 

the number of chiral carbons in 'A' are

(1) 1 $\qquad$ (2) 2

(3) 3 $\qquad$ (4) 4

5. $CH_3—CH{=}CH_2 \xrightarrow{dil/H_2SO_4} A$

$CH_3—CH{=}CH_2 \xrightarrow{B_2H_6} \xrightarrow[{}^-OH]{H_2O_2} B$

Wrong statement about the product is

(1) A and B have the same functional group

(2) A and B are position isomers.

(3) A and B show chain isomerism

(4) Mixed ether is the isomer of both A and B

6. Which of the following alkene is most reactive for hydration

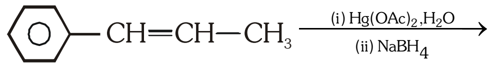
(1) ethene

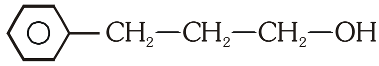
(2) propene

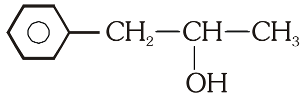
(3) 1–butene

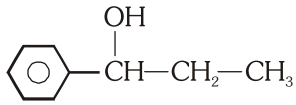
(4) 2–methyl propene

7. The major product of the following reaction is

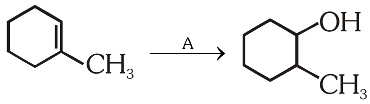


(1) 

(2) 

(3) 

(4) 

8.  ; Reagent 'A' is

(1) $BH_3/H_2O_2/\overset{\ominus}{O}H$

(2) $H_2O/H^{\oplus}$

(3) $Hg(OCOCH_3)_2/NaBH_4$

(4) Cl_2/aq. NaOH

9. Which of the following alkenes on hydration gives a tertiary alcohol

(1) 2–Butene $\qquad$ (2) Isobutylene

(3) Ethene $\qquad$ (4) α–Butylene

10. The predominant product formed when 3–methyl–2–pentene reacts with HOCl is

(1) $CH_3—CH_2—\underset{CH_3}{\overset{Cl}{C}}—\overset{OH}{C}H—CH_3$

(2) $CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\overset{OH}{C}H—CH_3$

(3) $CH_3—CH_2—\underset{CH_3}{\overset{Cl}{C}}—\overset{Cl}{C}H—CH_3$

(4) $CH_3—CH_2—\underset{CH_3}{\overset{OH}{C}}—\underset{Cl}{C}H—CH_3$

11. Propene on addition with HI, gives

(1) $CH_3—CHI—CH_3$

(2) $CH_3—CH_2—CH_2I$

(3) $CH_3—CHI—CH_2I$

(4) None of the above

12. What is the main product of this reaction?

$CH_3 - C \equiv CH \xrightarrow[\text{Excess}]{HCl(g)} ?$

(1) $CH_3 - \overset{\overset{Cl}{|}}{C} = CH_2$

(2) $CH_3 - \underset{\underset{Cl}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$

(3) $CH_3 - CH_2 - CH{<}^{Cl}_{Cl}$

(4) $CH_3 - \overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}} - CH_3$

13. Propan– 1–ol can be prepared from propene by
(1) H_2O/H_2SO_4
(2) $Hg(OAc)_2/H_2O_2$ followed by $NaBH_4$.
(3) B_2H_6 followed by H_2O_2.
(4) CH_3CO_2H/H_2SO_4

14. 3–Phenyl propene on reaction with HBr gives (as a major product)
(1) $C_6H_5CH_2CH(Br)CH_3$
(2) $C_6H_5CH(Br)CH_2CH_3$
(3) $C_6H_5CH_2CH_2CH_2Br$
(4) $C_6H_5CH(Br)CH{=}CH_2$

NUCLEOPHILIC ADDITION REACTION

15. Acetaldehyde reacts with semicarbazide, product will be :

(1) $CH_3CH{=}NNH{-}CO{-}NH_2$
(2) $CH_3CH{=}NCONHNH_2$
(3) $CH_3CH{=}NHNH_2$
(4) $CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CONH_2$

16. Cyanohydrin of the following compound on hydrolysis gives compound that can show optical isomerism :
(1) HCHO (2) CH_3CHO
(3) CH_3COCH_3 (4) All the above

17. In this reaction :
$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$
$\xrightarrow{H_2O} CH_3CH(OH)COOH$
an asymmetric centre is generated. The acid obtained would be :-
(1) D–isomer
(2) L–isomer
(3) 50% D + 50% L–isomer
(4) 20% D + 80% L–isomer

18. When two mole of alcohol reacts with 1 mole of ketone, it gives :-
(1) Hemiacetal (2) Acetal
(3) Hemiketal (4) Ketal

19. When acetone reacts with Grignard reagent followed by hydrolysis, it gives :
(1) 1° –alcohol (2) 2° –alcohol
(3) 3° –alcohol (4) Methyl alcohol

FREE RADICAL ADDITION REACTION

20. Reaction of HBr with propene in the presence of peroxide gives
(1) 3–bromo propane (2) Allyl bromide
(3) n–propyl bromide (4) Isopropyl bromide

21. Isobutene $\xrightarrow[H_2O_2]{HBr}$ "product". The product is

(1) Isobutyl bromide (2) Tert. butyl bromide
(3) Tert. butyl alcohol (4) isobutyl alcohol

FREE RADICAL SUBSTITUTION REACTION

22. Alkane reacts with which of the following halogens in dark
(1) F_2 (2) Cl_2 (3) I_2 (4) Br_2

23. The nitrating agent for the nitration of alkanes is:
(1) Conc. HNO_3
(2) Mixture of conc. HNO_3 and conc. H_2SO_4
(3) Acetyl nitrate
(4) HNO_3 vapours at high temperature

24. The chain propagating step is fastest in the reaction of an alkane with
(1) Fluorine free radical (2) Chlorine free radical
(3) Iodine free radical (4) Bromine free radical

25. In the nitration of propane, the product obtained in maximum yield is
(1) 1–nitropropane (2) 2-nitropropane
(3) Nitroethane (4) Nitromethane

26. Only two isomeric monochloro derivatives are possible for (exclude stereo isomers)
(1) n-butane
(2) 2, 4-dimethyl pentane
(3) benzene
(4) 2-methyl butane

27. What is the chief product obtained when n-butane is treated with bromine in the presence of light at 130°C ?

(1) $CH_3-CH_2-CH_2-CH_2-Br$

(2) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-Br$

(3) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Br$

(4) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-Br$

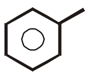
ELECTROPHILIC SUBSTITUTION REACTION

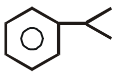
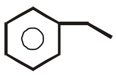
28. The strongest deactivating effect on aromatic ring is

(1) $-CH_2Cl$ (2) $-OCH_3$

(3) $-CH_3$ (4) $-CCl_3$

29. Which of the following is maximum reactive towards E.S.R. :-

(1)  (2) 

(3)  (4) 

30. Correct order of reactivity of following compound with an electrophile :-

(I) $p-CH_3-C_6H_4-CH_3$

(II) $C_6H_5-CH_3$

(III) $p-CH_3-C_6H_4-NO_2$

(IV) $p-O_2N-C_6H_4-NO_2$

(1) I > II > III > IV (2) II > I > IV > III

(3) III > II > I > IV (4) IV > III > II > I

31. Toluene is more reactive than benzene towards electrophilic reagents due to :-

(1) Inductive effect only

(2) Hyperconjugative effect only

(3) Both inductive as well as hyperconjugative effects

(4) Strong mesomeric effect

32. Nitration of benzene is

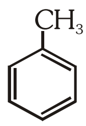
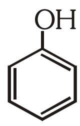
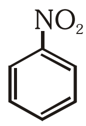
(1) nucleophilic substitution

(2) nucleophilic addition

(3) electrophilic substitution

(4) electrophillic addition

33. Consider the following compounds :

(I)  (II)  (III)  (IV) 

Correct order of their reactivity in electrophilic substitution reactions would be :-

(1) I > II > III > IV (2) IV > III > II > I

(3) III > II > I > IV (4) III > IV > I > II

34. The active species in the nitration of benzene is

(1) NO_2^+ (2) HNO_3

(3) NO_3^- (4) NO_2^-

35. The function of anhydrous $AlCl_3$ in the Friedel craft's reaction

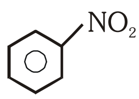
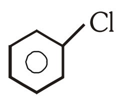
(1) To absorb water

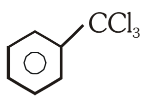
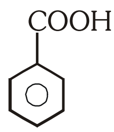
(2) To absorb HCl

(3) To produce electrophile

(4) To produce Nucleophile

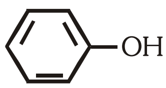
36. In which of the following compound the electrophile attack on o– and p– positions :

(1)  (2) 

(3)  (4) 

NUCLEOPHILIC SUBSTITUTION REACTION

37. The correct reactivity order of alcohols towards H–X will be

(I)  (II) $CH_2=CH-CH_2OH$

(III) CH_3-CH_2-OH (IV) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(1) II > I > III > IV (2) IV > III > II > I

(3) II > IV > I > III (4) II > IV > III > I

38. Which of the following product will be obtained when neopentyl alcohol is treated with conc. HCl in presence of $ZnCl_2$.

(1) t– butyl chloride (2) isobutylene

(3) t– pentyl chloride (4) Neo pentyl chloride

39. In S_N1 the first step involves the formation of
(1) free radical (2) carbanion
(3) carbocation (4) final product

40. To form alkane isonitrile, alkyl halide is reacted with:
(1) KCN (2) AgCN
(3) NaCN (4) NH_4CN

41. The most reactive towards S_N1 is
(1) $PhCH_2Cl$ (2) Ph Cl
(3) $PhCHCl(CH_3)$ (4) p- $NO_2C_6H_4CH_2Cl$

42. Alkyl fluorides are synthesised by
(1) Finkelstein reaction (2) Swart reaction
(3) Kolbe reaction (4) Wurtz reaction

43. The products of reaction of alcoholic silver nitrite with ethyl bromide are
(1) Ethane (2) Ethene
(3) Ethyl alcohol (4) Nitro ethane

44. For the reaction,
$C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$, the order of reactivity is
(1) HI > HCl > HBr
(2) HI > HBr > HCl
(3) HCl > HBr > HI
(4) HBr > HI > HCl

45. The reaction ,$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ obeys the mechanism
(1) S_N1 (2) S_N2
(3) E^1 (4) E^2

46. Butanenitrile may be prepared by heating
(1) Propyl alcohol with KCN
(2) Butyl alcohol with KCN
(3) Butyl chloride with KCN
(4) Propyl chloride with KCN

47. The given reaction is an example of
$C_2H_5Br + KCN(aq.) \longrightarrow C_2H_5CN + KBr$
(1) Elimination
(2) Nucleophilic substitution
(3) Electrophilic substitution
(4) Redox change

48. Most readily hydrolised halide is
(1) C_6H_5Cl (2) $(C_6H_5)_2CHCl$
(3) $C_6H_5CH_2Cl$ (4) $(C_6H_5)_3CCl$

49. An alkyl halide may be converted in to an alcohol by
(1) Addition (2) Substitution
(3) Dehydrohalogenation (4) Elimination

50. Compound is most reactive towards NaOH in
(1) CH_3Cl (2) $CH_2{=}CHCl$
(3) C_6H_5Cl (4) $C_6H_5CH_2Cl$

51. Most stable carbocation formed from $(CH_3)_3C-Br$, $(C_6H_5)_3CBr$, $(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be
(1) $C_6H_5\overset{\oplus}{C}H_2$ (2) $(CH_3)_3\overset{\oplus}{C}$
(3) $(C_6H_5)_3\overset{\oplus}{C}$ (4) $(C_6H_5)_2\overset{\oplus}{C}H$

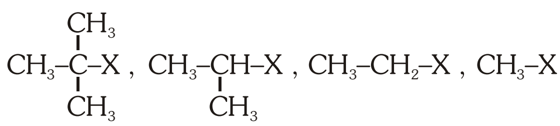
52. S_N1 reaction on optically active substrates mainly gives
(1) Retention in configuration
(2) Inversion in configuration
(3) Racemise product
(4) No product

53. The hydrolysis of alkyl halides by aqueous NaOH is best termed as
(1) electrophilic substitution reaction
(2) electrophilic addition reaction
(3) nucleophilic addition reaction
(4) nucleophilic substitution reaction

54. Reaction of sodium ethoxide and ethyl iodide will give :-
(1) Ether (2) Ethyl alcohol
(3) Acetaldehyde (4) Acetic acid

55. The least reactive chlorine is present in
(1) Methyl chloride (2) Allyl chloride
(3) Ethyl chloride (4) Vinyl chloride

56. Arrange the following compounds in the increasing order of their S_N^2 reactivity?



(a) (b) (c) (d)

(1) (a) < (b) < (c) < (d)
(2) (a) < (c) < (d) < (b)
(3) (d) < (c) < (b) < (a)
(4) (b) < (d) < (c) < (a)

57. Which alcohol produces turbidity with Lucas reagent most slowly
(1) 2–Butanol (2) t–Butyl alcohol
(3) Isobutyl alcohol (4) Diphenylcarbinol

58. The preparation of ethers from alcohols by using sulphuric acid is called :-
(1) Williamson's ether Synthesis
(2) Williamson's continuous etherification process
(3) Ziesel's method
(4) Zerewitinoff method

59. The reaction of ethyl iodide with sodium ethoxide is
(1) An electrophilic substitution reaction
(2) A nucleophilic addition reaction
(3) A nucleophilic substitution reaction
(4) A free radical substitution reaction

60. The Williamson synthesis involves :-
(1) A nucleophilic addition
(2) An electrophilic substitution
(3) SN^2 displacement
(4) SN^1 displacement

61. In the Williamson synthesis of ethers given by the general equation –

$R—X + R'ONa \longrightarrow R—O—R'$ the yield from R—X follows the sequence :-
(1) $CH_3X > 1° > 2° > 3°$
(2) $CH_3X < 1° < 2° < 3°$
(3) $CH_3X < 1° < 2° > 3°$
(4) $CH_3X > 1° < 2° < 3°$

62. With conc. HBr ethyl phenyl ether yields :–
(1) Phenol and ethyl bromide.
(2) Bromobenzene and ethanol
(3) Phenol and ethane
(4) Bromobenzene and ethane

63. An unknown alcohol is treated with the "Lucas reagent' to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism :-
(1) secondary alcohol by SN1
(2) tertiary alcohol by SN1
(3) secondary alcohol by SN2
(4) tertiary alcohol by SN2

ELIMINATION REACTION

64. The reactivity of alkyl halides in E^2 elimination reactions follows the order
(1) R–I < R–Br < R–Cl < R–F
(2) R–F < R–Cl < R–Br < R–I
(3) R–I > R–Cl > R–Br < R–F
(4) R–I < R–Br < R–F < R–Cl

65. The unimolecular elimination involves formation of
(1) A free radical (2) A carbanion
(3) A carbocation (4) A biradical

66. Which of the following alkyl bromides will eliminate HBr fastest
(1) Ethyl bromide (2) Propyl bromide
(3) Isopropyl bromide (4) t-Butyl bromide

67. 1–phenyl-2-chloropropane on treating with alc. KOH gives mainly :
(1) 1-phenylpropene
(2) 2-phenylpropene
(3) 1-phenylpropan-2-ol
(4) 1-phenylpropan-1-ol

68. Which of the following alkyl halides gives a mixture of alkenes on dehydrohalogenation
(1) n–Propyl halide
(2) Isopropyl halide
(3) s–Butyl bromide
(4) t–Butyl bromide

69. Arrange the following alkanols A, B and C in order of their reactivity towards acid catalysed dehydration:-

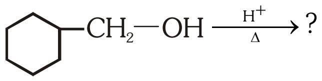
(A) $CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—CH_2—OH$

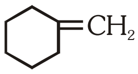
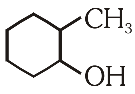
(B) $CH_3—\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—CH_3$

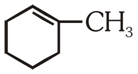
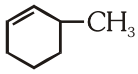
(C) $CH_3—\overset{\overset{CH_3}{|}}{CH}—\overset{\overset{OH}{|}}{CH}—CH_3$

(1) A > B > C (2) B > A > C
(3) B > C > A (4) C > B > A

70. The major product in the following reaction is



(1)  (2) 

(3)  (4) 

71. The major product obtained from the heating of 3,3–dimethyl –1– butanol with H_2SO_4 is

(1) 3, 3–dimethyl–1–butene

(2) 2, 3–dimethyl–2–butene

(3) 2, 3–dimethyl–1–butene

(4) cis and trans isomers of product (2)

72. Arrange the following alkyl halides in decreasing order of the rate of elimination reaction with alcoholic KOH.

(A) $CH_3\text{–}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}\text{–}CH_2\text{–}Br$ (B) $CH_3\text{–}CH_2\text{–}Br$

(C) $CH_3\text{–}CH_2\text{–}CH_2\text{–}Br$

(1) A > B > C (2) C > B > A

(3) B > C > A (4) A > C > B

EXERCISE-I (Conceptual Questions) **ANSWER KEY**

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	3	2	3	4	3	1	2	4	1	4	3	2	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	3	4	3	3	1	1	4	1	2	1	2	4	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	3	1	3	2	4	3	3	2	3	2	4	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	2	4	2	4	3	3	4	1	4	1	3	2	3	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72			
Ans.	1	1	2	2	3	4	1	3	3	3	2	4			

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. ***Assertion :–*** trans 2-butene gives racemic mixture when treated with Cl_2.
Reason :– Addition of Cl_2 is anti.
(1) A (2) B (3) C (4) D

2. ***Assertion :–*** Addition of HBr in presence of peroxide on alkene is free radical addition. This reaction is not shown by HCl.
Reason :– Due to less bond energy of HCl than HBr, homolysis of HCl can not occurs.
(1) A (2) B (3) C (4) D

3. ***Assertion :–*** Additon of $CBrCl_3$ in presence of peroxides takes place faster to 2-ethyl-1-hexene than to 1-octene.
Reason :– Intermidiate free radical in case of 2-ethyl-1-hexene is more stable.
(1) A (2) B (3) C (4) D

4. ***Assertion :–*** Ketone gives 2.4-DNP test easily than aldehyde.
Reason :– Ketone is more reactive than aldehyde.
(1) A (2) B (3) C (4) D

5. **Assertion :-** p-nitrophenol gives more electrophilic substituted compound than m-methoxy phenol
Reason :- Methoxy group shows only negative I-effect
(1) A (2) B (3) C (4) D

6. ***Assertion*** : Rates of nitration of benzene and hexadeuterobenzene are different.
Reason : C–H bond is stronger than C–D bond.
(1) A (2) B (3) C (4) D

7. ***Assertion :–*** Major product obtained from FCR of benzene with n-butyl chloride is tert. Butyl benzene.
Reason :– Intermediate 1^0 carbocation rearrangements in more stable 3^0 carbocation.
(1) A (2) B (3) C (4) D

8. ***Assertion :–*** When CH_3Cl and $AlCl_3$ are used in F.C.R. the electrophile is $Cl^{\oplus}$.
Reason :– The first attack on benzene is of $Cl^{\oplus}$.
(1) A (2) B (3) C (4) D

9. ***Assertion :–*** The correct reactivity order towards sulphonation is –
meta xylene > Toluene > chlorobenzene
> Nitrobenzene
Reason :– m-xylene has the highest electron density & hence most reactive.
(1) A (2) B (3) C (4) D

10. ***Assertion :–*** Iodine monochloride (ICl) reacts with benzene in presence of a lewis acid such as anhyd. $AlCl_3$ to give iodobenzene and not chlorobenzene.
Reason :– Iodine is less electronegative than chlorine in the reaction.
(1) A (2) B (3) C (4) D

11. ***Assertion :–*** Vinyl halides can not be used in place of alkyl halides in friedal crafts alkylation.
Reason :– Vinyl halides does not give electrophile easily.
(1) A (2) B (3) C (4) D

12. ***Assertion :-*** If the hydrogen atoms of benzene are replaced by deuterium atoms then the reactivity of benzene ring is decreased for ESR.
Reason :- The bond strength of C–D is more than C–H and reaction depends on the bond strength of C–D and C–H.
(1) A (2) B (3) C (4) D

13. ***Assertion :–*** Benzyl chloride is more reactive than p–chloro toluene towards aqueous NaOH.
Reason :– The C–Cl bond in benzyl chloride is more polar than C–Cl bond in p–chloro toluene.
(1) A (2) B (3) C (4) D

14. ***Assertion :–*** $CH_3CH_2OCH_2Cl$ reacts faster when

(1) A (2) B (3) C (4) D

15. ***Assertion :-*** p–Chloro aniline and aniliniumchloride can be distinguished by $AgNO_3$.
Reason :- p–Chloro aniline is less basic than aniline.
(1) A (2) B (3) C (4) D

16. ***Assertion :-*** Phenoxide ion is a poor nucleophile than a methoxide ion.
Reason :- In methoxide ion oxygen is attached to sp^3 carbon.
(1) A (2) B (3) C (4) D

17. **Assertion :-** $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-Br + NaOH$

$\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-OH$ (major)

Reason :- It follows with formation of more stable carbanion
(1) A (2) B (3) C (4) D

18. ***Assertion :-*** Aryl sulphonic acid gives phenol on reacting with NaOH at high temperature followed by :
Reason :- This acidification reaction is electrophillic substitution reaction.
(1) A (2) B (3) C (4) D

19. ***Assertion :–*** Aryl halides are more reactive than alkyl halide towards NSR.
Reason :– Intermediate carbocation is more stable obtained from Aryl halide.
(1) A (2) B (3) C (4) D

20. ***Assertion :–*** In SN^1 reaction if the alkyl halide is optically active then the product is recemic mixture.
Reason :– All tertiary halides gives racemic mixture.
(1) A (2) B (3) C (4) D

21. ***Assertion :–*** Chlorobenzene does not react with NaOH where as ethyl chloride reacts.
Reason :– The partial double bond between C and Cl causes less reactivity towards nucleophilic substitution.
(1) A (2) B (3) C (4) D

22. ***Assertion :–*** Benzyl bromide when kept in acetone water it produces benzyl alcohol.
Reason :– The reaction follows SN^2 mechanism
(1) A (2) B (3) C (4) D

23. ***Assertion :–*** Anisole on reaction with HI gives phenol and CH_3I.
Reason :– Phenyl-oxygen bond is stronger than methyl-oxygen bond in anisole and hence is not cleaved by HI.
(1) A (2) B (3) C (4) D

24. ***Assertion :–*** In Lucas test, 3° alcohols react immediately.
Reason :– An equimolar mixutre of anhydrous $ZnCl_2$ and conc. HCl is called Lucas reagent.
(1) A (2) B (3) C (4) D

25. ***Assertion :–*** t-butyl methyl ether is prepared by reaction of t-butyl bromide with methoxide ion.
Reason :– Reaction follow SN^2-mechanism.
(1) A (2) B (3) C (4) D

26. ***Assertion :–*** Treatment of 1,3-dibromopropane with zinc dust produces cyclopropane.
Reason :– The reaction of alkyl halide with Zn dust is nucleophilic substitution.
(1) A (2) B (3) C (4) D

27. ***Assertion :–*** 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 2–butene as a major product.
Reason :– 2-Butene is more stable than 1-butene.
(1) A (2) B (3) C (4) D

28. ***Assertion :-*** Aldehyde are more reactive than Ketone.

Reason :- Nucleophilic addition reaction in carbonyl compound

$\propto = \dfrac{1}{\text{Steric hindrence}}$ and $\propto$ positive charge at carbon of carbonyl group.

(1) A (2) B (3) C (4) D

29. ***Assertion :-*** $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle Cl}{\overset{|}{CH}}-CH_3 \xrightarrow{\text{alc. KOH}/\Delta}$

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3 + CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2$

(Major)

Reason :- In E_2 reaction product formation always takes place by saytzeff rule.

(1) A (2) B (3) C (4) D

30. ***Assertion :-*** The product of reaction of 2-Methyl cyclo hexanol with HBr at room temperature is 1-Bromo-1-methyl cyclo hexane.

Reason :- Generally dehydration occur and product is 1-methyl cyclo hexene.

(1) A (2) B (3) C (4) D

31. ***Assertion :-*** Compound $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$ can not give ether with conc. H_2SO_4.

Reason :- It favours the formation of alkene over ether.

(1) A (2) B (3) C (4) D

32. ***Assertion :-*** In friedel craft's reaction of 1-chloropropane gives isopropyl benzene as product.

Reason :- The primary carbocation rearranges to form secondary carbocation.

(1) A (2) B (3) C (4) D

33. ***Assertion :-*** Propene reacts with diborane to form tripropyl borane.

Reason :- It follows anti markowni koff's rule.

(1) A (2) B (3) C (4) D

34. ***Assertion :-*** 2-Bromopentane react with alcoholic KOH to form 2-pentene.

Reason :- Alcoholic KOH follows E_1, mechanism.

(1) A (2) B (3) C (4) D

35. ***Assertion :-*** p-Nitrobenzyl ethyl ether on heating with conc. HBr and gives p-Nitrobenzyl bromide.

Reason :- p-Nitrobenzyl carbocation is highly stable.

(1) A (2) B (3) C (4) D

36. ***Assertion :-*** Phthalic anhydride react with phenol in presence of NaOH gives pink colour.

Reason :- It forms phenolpthalein.

(1) A (2) B (3) C (4) D

37. ***Assertion :-*** Benzophenone on reaction with $NaHSO_3$ gives stable addition product.

Reason :- Equilibrium of this reaction lies on the right side.

(1) A (2) B (3) C (4) D

38. ***Assertion :-*** C_6H_5MgBr on reaction with CO_2 gives benzoic acid

Reason :- CO_2 is a good electrophile

(1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**4**	**3**	**1**	**4**	**4**	**4**	**4**	**4**	**1**	**1**	**1**	**4**	**1**	**1**	**2**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**2**	**4**	**3**	**4**	**3**	**1**	**3**	**1**	**2**	**4**	**3**	**1**	**1**	**3**	**3**
Que.	31	32	33	34	35	36	37	38							
Ans.	**1**	**1**	**3**	**3**	**3**	**1**	**4**	**3**							